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THE

SCIENTIFIC PROCEEDINGS

OF

THE ROYAL DUBLIN SOCIETY.

No. 1.

AWARD OF THE BOYLE MEDAL FOR PURE SCIENCE

TO WILLIAM RINGROSE GELSTON ATKINS, O.B.E., Sc.D., F.I.C., F.R.S. 1928.[1]

REPORT OF THE COMMITTEE OF SCIENCE AND ITS INDUSTRIAL APPLICATIONS.

ATKINS' earliest work in chemistry was concerned with the problem of molecular association and the formation of easily dissociable molecular compounds. To this end he carried out researches upon the cryoscopic, ebullioscopic, and association constants of trimethylcarbinol. Similar work was carried out later in conjunction with Professor E. A. Werner, Miss K. Shipsey, and the late T. A. Wallace upon thio-urea and various alcohols. With his friend Wallace, Atkins prepared pure allyl alcohol by distilling the aqueous alcohol with benzene, and later, in connection with war service, he applied the method of fractional distillation to the examination of the complex mixtures containing ketones, which were being tested as to their suitability as solvents for acetyl cellulose used in aeroplane varnishes. Problems of fractional distillation also presented themselves in relation with the use in aero-engines of petrols from diverse sources.

In connection with his father's surgical work, Atkins undertook the cryoscopic examination of the blood and urine of patients in various stages of kidney disease. The results were interpreted according to the work of Koranyi, as evidence for or against the removal of the kidney. Freezing point determinations were also applied to other physiological liquids, and were continued with Professor H. H. Dixon in a series of researches, using in them the method

[1] The Medal was awarded by the Council of the Royal Dublin Society on January 19th, 1928. The presentation was made at a special Scientific Meeting on February 15th, 1928, when the Medal was handed to Dr. Atkins by Professor J. Joly, SC.D., F.R.S., F.T.C.D., Senior Vice-President of the Society.

of thermo-electric cryoscopy developed by the latter. Results of high value in vegetable physiology were obtained.

Observation of the changes in colour undergone by the sap expressed for cryoscopic examination led him to a study of oxidase action and of the distribution of oxidases in plants, notably in the species of the genus Iris and in algae. An attempt to ascertain the amounts of the various solutes giving rise to the osmotic pressure of the expressed sap led to an investigation of the methods of estimation of plant sugars, and a most useful method of estimation was evolved, depending on their varying resistance to oxidation by bromine. This work Atkins carried out in collaboration with Miss E. G. Wilson, with whom he later studied methods for the estimation of the traces of the compounds of phosphorus, arsenic, and silicon found in sea water.

The continuance of the war, however, diverted his attention to other work at Woolwich Arsenal, the National Physical Laboratory, and in the Royal Flying Corps, in Egypt. Varied problems connected with the materials used in aeroplanes and balloons had to be studied, especially those concerning the effect of sunlight on linen and on rubber-coated cotton fabrics, and those concerning the stability of lubricants under the severe working conditions of the air-cooled aero-engine.

After the war the interest aroused in lubricants led to the preparation of several papers on their examination and on the miscibility relations of the constituents of petrol with castor oil. Then he turned to the measurement of hydrogen ion concentrations in relation to the solubility of inorganic salts, to physiological liquids, and to soil solutions. He continued this work in India, and later at Plymouth, and obtained additional evidence supporting the views put forward by Wherry in the United States as to the large part played in plant distribution by the acidity or alkalinity of the soil. He also elucidated the relation of the hydrogen ion concentration to the flower colour of Hydrangea, for only in acid soils is there a sufficiency of iron salts to produce the blue colour; the plant when grown on alkaline soils having pink flowers.

He showed that the colorimetric estimation of hydrogen ion concentration is suitable for a study of the photosynthetic changes in sea water, and by this method he was able to obtain an estimate of the minimum annual phytoplankton crop.

The estimation of the phosphate and silicate content of sea water led to far-reaching results. Atkins showed that practically all the phosphate available in the surface water at the beginning of the growing season is, at its close, incorporated in the phytoplankton. Hence the lack of phosphate is a factor limiting plant growth, and consequently animal growth, in the sea. He found that the depths of the ocean, where light is inadequate for the persistence of plant-life, are at all times rich in phosphates, and yield up their treasure where deep currents encountering banks up-well, or when temperature changes result in vertical mixing. These observations and deductions have obviously important bearings on the fishing industry and on food production, in addition to their great biological interest.

The desire to study the depth to which the illumination was adequate for plant growth led to a partnership with Dr. H. H. Poole, who devised a photo-electric photometer suitable for work on a small trawler throughout the year. This apparatus has since been used for the measurement of the illumination in a wood and in shady places, in connection with a study of plant distribution.

The study of fabric for war work led Atkins later to the study of methods of preserving fishing nets by various means, and he obtained results of great value by the use of copper soaps dissolved in petrol.

In his book, "Researches in Plant Physiology," Atkins has shown himself a scientific writer of exceptional ability. In it he has summarized some of his researches, and discussed their bearing on many of the problems of vegetable physiology.

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No. 2.

AWARD OF THE BOYLE MEDAL FOR APPLIED SCIENCE

TO WALTER ERNEST ADENEY, D.Sc., F.R.C.Sc.I., F.I.C.

1928.[1]

REPORT OF THE COMMITTEE OF SCIENCE AND ITS INDUSTRIAL APPLICATIONS.

THE work of Professor Adeney has principally been devoted to fundamental research in the important problems arising out of the discharge of sewage and waste products into rivers and tidal estuaries. The growth of industrialism had already, in 1868, rendered the question of river pollution so pressing that a special Commission was appointed to deal with the matter. At that time the process of fermentation was only beginning to receive attention at the hands of Pasteur, and the problem of the change in sewage matter, when mixed with river water, was regarded as a problem in pure chemistry. The presence of carbon dioxide, as the end product of organic oxidation, was selected as the criterion of natural purification of streams. The method employed in testing for it was not, however, sufficiently delicate to detect the very small quantities in which it is formed during natural purification, and the investigations of this special Commission led to the imposition on local authorities of an excessively high standard of purification of sewage matter, before entering natural waters, which would have been a costly burden if it had not been largely disregarded in practice.

Again, in 1898, the treatment and disposal of sewage matter was referred to the Royal Commission on Sewage Disposal for further inquiry. Sir William Tilden records in his life of Sir William Ramsay that Dr. Adeney's original work, done before the Commission came into existence, was of fundamental importance, and was only extended and amplified by the investigations made by the Commission. An account of this work was communicated to the Royal Dublin Society in 1895 in a paper entitled "The Course and Nature of the Fermentative Changes in Natural and Polluted Waters and in Artificial Solutions as indicated by the Composition of the Dissolved Gases." It took the view that the oxidation of organic matter in water must be regarded as mainly the result of the biochemical action of minute bacteria, which feed upon the

[1] The Medal was awarded by the Council of the Royal Dublin Society on January 19th, 1928. The presentation was made at a special Scientific Meeting on February 15th, 1928, when the Medal was handed to Professor Adeney by Professor J. Joly, SC.D., F.R.S., F.T.C.D., Senior Vice-President of the Society.

sewage in the presence of an excess of dissolved oxygen. By means of an improved technique in the extraction and estimation of the dissolved oxygen and of carbon dioxide in water polluted by sewage matter in solution and in the colloidal state, Dr. Adeney was able to analyse thoroughly the chemical changes which accompany the destruction of noxious organic products in rivers. It was shown that there were two distinct and progressive stages of bacterial fermentation: the first or carbon stage, dominated by the formation of carbon dioxide, ammonia, and coloured organic material termed "humus"; the second or nitrogen stage, in which the colouring matter takes part in the fermentation of ammonia to nitrates. Offensive putrefactive products are only formed during the first stage when the supply of dissolved oxygen becomes exhausted.

The Commission accepted the general conclusions of these investigations, and, in the light of more complete knowledge, were able to lay down less exacting and more economical standards for sewage effluents than the Commission of 1870, as given in the Eighth Report, issued in the year 1912. They depend upon "tests which are based upon the rate and degree of absorption of oxygen, and which are the most trustworthy for determining whether a nuisance is, or is not, likely to be caused in a stream by discharge of sewage liquids."

The rate of supply of oxygen had thus been shown to be a factor of prime importance in the natural or self-purification of rivers. From 1905 onwards the attention of Dr. Adeney has, therefore, been directed towards the problem of the mechanism of the aeration of water, and his principal aim has been to devise experiments from which it would be possible to draw conclusions applicable to natural conditions in the open air. Gases can pass into solution in liquids either by the extremely slow process of diffusion through a quiescent surface into a mass of liquid free from convection currents or other disturbances, or by the rapid method of agitation and shaking. In an endeavour to approximate to natural conditions (which must lie between these limits), by drawing a current of air over the surface of columns of water maintained as far as possible at a constant temperature, Dr. Adeney discovered the phenomenon of "streaming."

The liquid at the surface, as it absorbs the air, streams downwards and sets up a very efficient process of mixing, so that the concentration of oxygen was found to be uniform to a depth of 10 feet. A thorough investigation of this phenomenon was carried out by Dr. Adeney, in collaboration with his colleague, Dr. A. G. G. Leonard, and Miss A. M. Richardson, Research Student. It was shown to arise from the cooling of the surface layer by evaporation in the current of air. The density increased, and the surface layer sank, setting up imperceptible streamlets of convection in the liquid.

These results have been confirmed in an interesting way by Dr. J. Newton Friend, in his study of the rusting of iron in water. The corrosion of iron acts as a delicate indicator of the concentration of the oxygen. The presence of streaming was made manifest by "vertical streaks of rust, more or less parallel with one another, and extending down the metal." Water exposed to dry air was twice as corrosive as that exposed to air saturated with aqueous vapour. This result is entirely in harmony with the work of Adeney and the convection

explanation, since the cooling effect of dry air in producing evaporation and consequent convection is very much greater than that of saturated air.

This discovery of "streaming" was of great assistance in clarifying the discussion of the practical problem of the aeration of water in nature, as it supplied an efficient mechanism of mixing, even in quiescent waters, which is, of course, supplemented by surface turbulence and the effects of currents in flowing water. But the rate of aeration had yet to be determined, independent of evaporation and downward streaming.

This was accomplished in a simple manner by enclosing a bubble of air of known volume in a long narrow tube. By causing it to ascend through the water column, the water flowed down the sides of the tube and over the bubble, exposing each portion of the water in a thin fresh film to the air, so that the maximum absorption took place. The results of the application of this method are recorded in three communications to the Royal Dublin Society by Adeney and the late H. G. Becker, then a research student in the Royal College of Science (1917–1920), entitled "Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water."

The measurements were made step by step. After two ascents of the tube, the fall in the pressure in the bubble was measured, from which the quantity of air absorbed could be determined. The air was then renewed, and the pressure restored to normal. The accuracy with which these measurements were carried out was demonstrated by the agreement of the sum total of these step-by-step measurements with the results of chemical analysis.

The observations were found to lie on an exponential curve, whose constants were determined. It thus was possible to calculate the maximum rate of aeration attainable for any volume of water under ideal conditions. Similar methods of calculation were applied to observations of absorption due to simple streaming from a calm surface. The rate of aeration in this case was 100 times slower. In his endeavour to approximate to natural conditions, Dr. Adeney studied the aeration when the surface was kept continuously disturbed. He found that sea water absorbed oxygen and nitrogen at but half the speed of the bubble experiment, while the rate in fresh water was reduced to one-fourth.

The importance of this work of Dr. Adeney, which we have just surveyed, lies chiefly in the fact that in the processes of biochemical oxidation of organic matter, such as are involved in the natural purification of streams and in many artificial methods of sewage treatment, the rate of aeration is virtually the limiting factor determining the rate of purification. The experiments of Dr. Adeney have provided the data by which the efficiency of various working processes can be judged, and have established the ideal conditions for the attainment of the maximum rate of aeration.

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1894. Note on the Present Condition of Water in the Reservoir at Roundwood.
On the Reduction of Manganese Peroxide in Sewage.

1895. The Course and Nature of Fermentative Changes in Natural and Polluted Waters, and in Artificial Solutions, as indicated by the Composition of the Dissolved Gases.
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Part 2.—Experiments with difficultly Fermentable Substances.
Part 3.—Bearing of the foregoing Experiments on the Analysis of Potable and Polluted Waters.
Part 4.—Humus: its Formation and Influence in Nitrification (1896).
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This paper was awarded the Mullins Gold Medal of the Institution of Civil Engineers of Ireland.

1898. Part 2. Sewage Sludges.

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1901. (With W. Kaye Parry.) The Discharge of Sewage into a Tidal Estuary.

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1905. Chemical Changes attending the Aerobic Bacterial Fermentation of Simple Organic Substances. Part 1—Urea, Asparagine, Albumose, and Rochelle Salt.

1906. The Composition of a Nitrogen Mineral Water at St. Edmundsbury, Lucan.

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1908. Section 1. Nature and Rate of the Chemical Changes which occur in Polluted Fresh and Salt Waters; and the Rate of Aeration of Fresh and Salt Water.

Section 2. B. The Estuary of the River Liffey (Dublin).
D. The River Humber and its Tributaries.
E. The Manchester Ship Canal.
F. The River Eden and Carlisle.
G. The Estuaries of the Rivers Plym and Tamar, and Plymouth.
H. The River Thames.

Addendum to Section 1.

Capacities of Fresh Water and of Sea Water to bear Pollution within Limits of Fouling.

No. 3.

A SIMPLE FORM OF PHOTO-ELECTRIC PHOTOMETER, USING A NEON LAMP TO MEASURE THE CURRENT.

By J. H. J. POOLE, Sc.D.

[Read April 24. Published separately May 18, 1928.]

In 1922 Messrs. Pearson and Anson (Proc. Phys. Soc., xxxiv, p. 204) showed that if an ordinary Osglim Neon lamp was connected in series with a high tension battery and a high resistance, and a suitable condenser connected across the terminals of the lamp, then the discharge through the lamp was not continuous, but consisted of a series of uniformly timed flashes. They further proved that the period of the flashes was approximately proportional to the product of the resistance and the capacity for any given lamp and voltage. Since this date much work has been carried out on this and similar phenomena in discharge tubes. For the most recent work on the subject, and also for a fairly complete bibliography, the reader may be referred to two papers in the *Philosophical Magazine* for November and December, 1927, by William Clarkson, M.Sc. Neglecting the discharge period, he shows that the time of flash T is given by $T = K(v_m - V_N) / C$ where C is the charging current, v_m the potential at which the discharge starts, V_N the potential at which it stops, and K the capacity.

This equation gives us a very convenient method of measuring photo-electric currents, for it is only necessary to substitute the photo-electric cell for the high resistance in series with the neon lamp, when the number of flashes per unit time observed in the lamp will obviously be some function of the quantity of illumination falling on the cell. The form of this function will depend on the characteristics both of the cell and the lamp. If we use a vacuum photo-electric cell, owing to the fact that the sensitivity of the cell does not change very rapidly with change of voltage across it, and that for constant voltage the current is proportional to the illumination, the charging current C should also be proportioned to the illumination. It does not follow, however, that the number of flashes per minute in the lamp will be proportional to the illumination, as v_m and V_N have been shown to be functions both of K and C, and hence it has been necessary to investigate the behaviour of the arrangement further. It has been found that as long as K is constant, and T varies from about 20″ to about 0·5″, then $v_m - V_N$ is a constant independent of C. If K is changed, however, $v_m - V_N$ also changes, apparently decreasing as K increases. This

observation agrees with previous work. (See Appleton, Emélius, and Barret, Proc. Camb Phil. Soc., xxii, p. 434, 1924.)

Fig. 1 shows diagrammatically the arrangement used in the investigation. As a source of voltage four 66-volt dry cell batteries were used. The photo-electric cell first tested was a sodium vacuum cell supplied by the G. E. C. Research Laboratories. To measure the current a resistance of 100,000 ohms was placed in series with the cell and lamp, and the potential drop across it measured with a Tinsley Potentiometer and a sensitive, high resistance, moving coil galvanometer. By this means currents down to about 10^{-9} amp. could be measured. The photo-electric cell was illuminated with a gas-filled 500 watt Ediswan Lamp. The lamp was suspended over the cell in such a way that its distance from the cell could be conveniently altered.

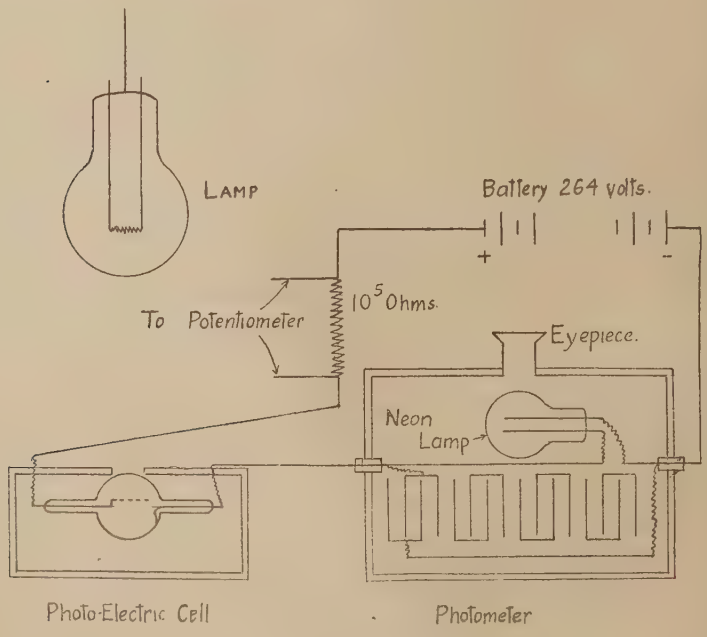


Fig. 1.

The neon lamp and its shunting capacity were both placed in a light-tight box. The flashes in the lamp could be observed through an eyepiece on the top of the box. It is essential that as little external light as possible should fall on the lamp, as the value of $v_m - V_N$ is decreased by direct illumination of the lamp (Oschevald and Turrant, Proc. Phys. Soc., xxxiv, p. 241, 1924). This is also necessary in order to render the very feeble flashes, obtained when the shunting capacity is small, visible.

It is plain that the equation $T = K\ (v_m - V_N / C$ is only an approximate one, as during the dark periods there must be a certain small current through the lamp. If the photo-electric current does not exceed this, we will get no flashes in the lamp at all. Fortunately, however, the results seem to show that, for the lamp I have used, this dark current must be small, as, within the limits of accuracy obtainable by this method, the current is proportional very nearly to the number of flashes per minute. The leakage through the shunting condenser is, as a matter of fact, much more troublesome, and in order to reduce it as far as possible, it was found necessary to arrange that no ebonite insulation should be used anywhere in the circuit. It is also necessary, of course, to remove the brass cap and ballasting resistance from the neon lamp, and then carefully clean off any of the cementing material still adhering to the glass, as its presence may spoil the insulation.

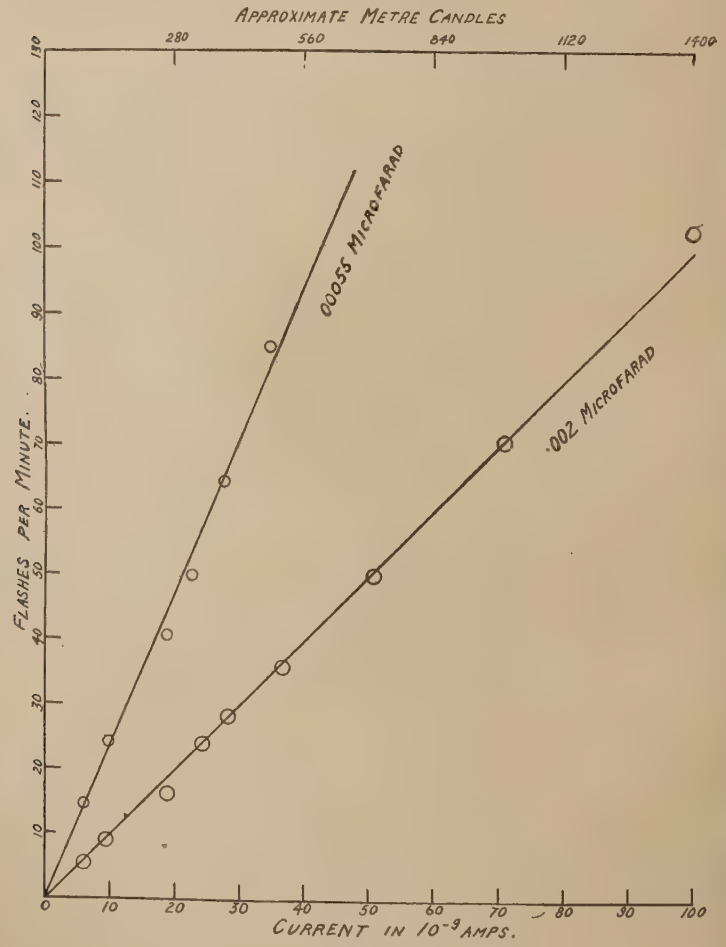
As it is hoped to use this arrangement for measuring daylight illumination under varying conditions, it is essential that it should have a very large range. This can be easily attained by varying the size of the shunting condenser. In the photometer described in this paper, four separate mica condensers ranging from ·00055 m.f. to ·05 m.f. were contained in the light-tight photometer box. These condensers were embedded in paraffin wax to reduce leakage, and it was arranged that any desired condenser could be quickly connected across the terminals of the neon lamp by a simple wander plug plan. In future models it will probably be better to use rather larger condensers, as the flash from the smallest condenser is very feeble and rather hard to observe, while in direct sunlight even the biggest condenser would flash too rapidly for visual timing. The constants of the photometer will depend on the neon lamp used, and hence if this lamp is altered the photometer will have to be re-standardised. The lamp used in these experiments was an Osglim Neon Letter lamp, one electrode being L shaped. This electrode was connected directly to the negative pole of the battery.

The following table shows the behaviour of the photometer for various illuminations. As the light from the gas-filled lamp is not nearly so blue as daylight, and the sodium cell is much more sensitive to the blue end of the spectrum, I have worked out the tables on the assumption that the candle-power of the lamp is about 250. Four 66-volt dry batteries were employed, the nominal voltage thus being 264 volts. When measured, however, by a voltmeter of about 20,000 ohms resistance, the voltage they gave was about 10 volts less. Unfortunately no reliable electro-static voltmeter of suitable range was available. The number of flashes per minute given for each illumination is the mean of four or five observations, as the individual observations may vary by seven or eight per cent. To save repetition, I have only given the figures for one value of the shunting capacity, as the results for the other values are similar.

TABLE I.

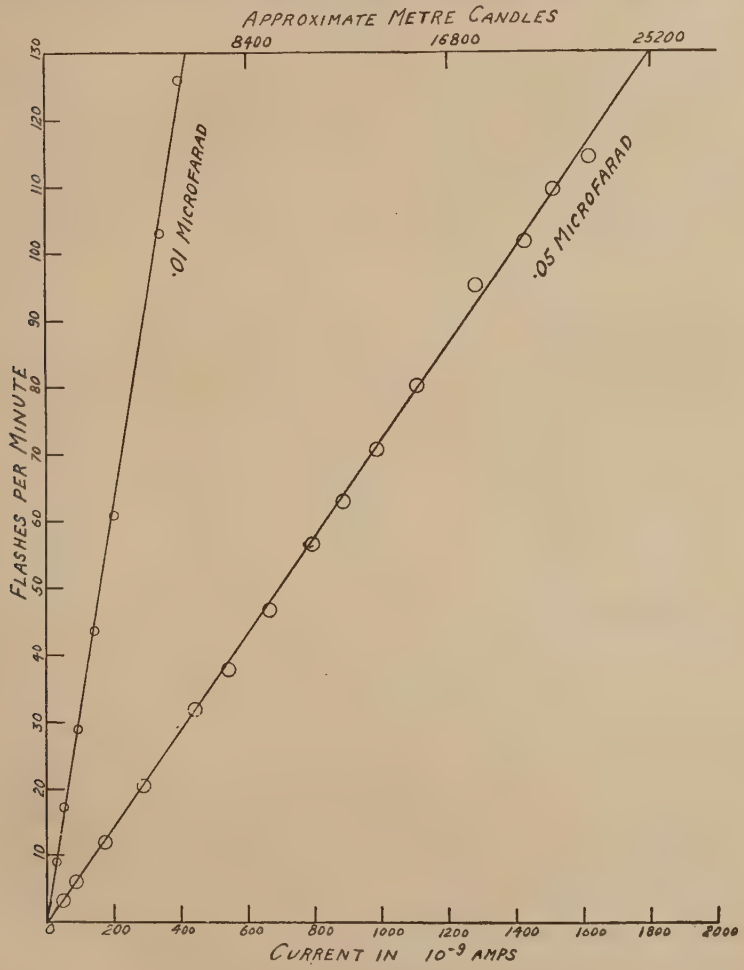
Light in metre candles . . .	62	111	250	309	391	510	695	1000	1560
Current in 10^{-9} amps. . . .	6·0	9·5	19·0	24·5	28·5	37·0	51·0	71·0	110
Flashes per minute . . .	5·5	9·0	16·4	24·1	28·3	36·0	49·6	70·4	113
Light ÷ Current	11·3	12·3	13·2	12·7	13·7	13·8	13·7	14·1	14·2
Current ÷ flashes per minute .	1·09	1·06	1·15	1·02	1·01	1·03	1·03	1·01	0·98

Shunting capacity = ·002 microfarad. Voltage of battery = 264.



GRAPH 1.

It will be observed that the current is not exactly proportional to the illumination. The sensitivity of the cell decreases with increasing illumination. Too much stress cannot, however, be laid on this point, as the illumination is only calculated from the approximate distance of the lamp filament from the cell, and as this is a rather uncertain quantity, the exact value of the illumination



GRAPH 2.

will also be uncertain. The flashes per minute are, however, very fairly proportional to the current, especially for values above about 25 flashes per minute. In using the photometer for daylight measurements, the small inaccuracies shown would be quite insignificant compared with the variations introduced by small alterations in the orientation of the photo-electric cell.

To illustrate the behaviour of the photometer with the other values of the capacity, graphs of the number of flashes per minute against the current have been plotted. In the case of the highest value of the capacity the artificial light available was not sufficiently strong, and daylight in this climate is too uncertain to use to illuminate the photo-electric cell. It was accordingly necessary to use a diode valve instead of the photo-electric cell to limit the charging current. This curve consequently only indicates how far the neon lamp can be trusted as a micro-ammeter. It is, however, probably correct to assume that even for the very strong illuminations required to give these currents from the photo-electric cell, the current would still be proportional to the illumination. The approximate values of the illumination have been marked on the curves on this assumption.

Table II gives finally the constants of the photometer, as calculated from the graphs for the various capacities.

TABLE II.

N = flashes per minute. Current = $aN \times 10^{-9}$ amps.
Illumination = bN metre candles. K = shunting capacity in microfarads.

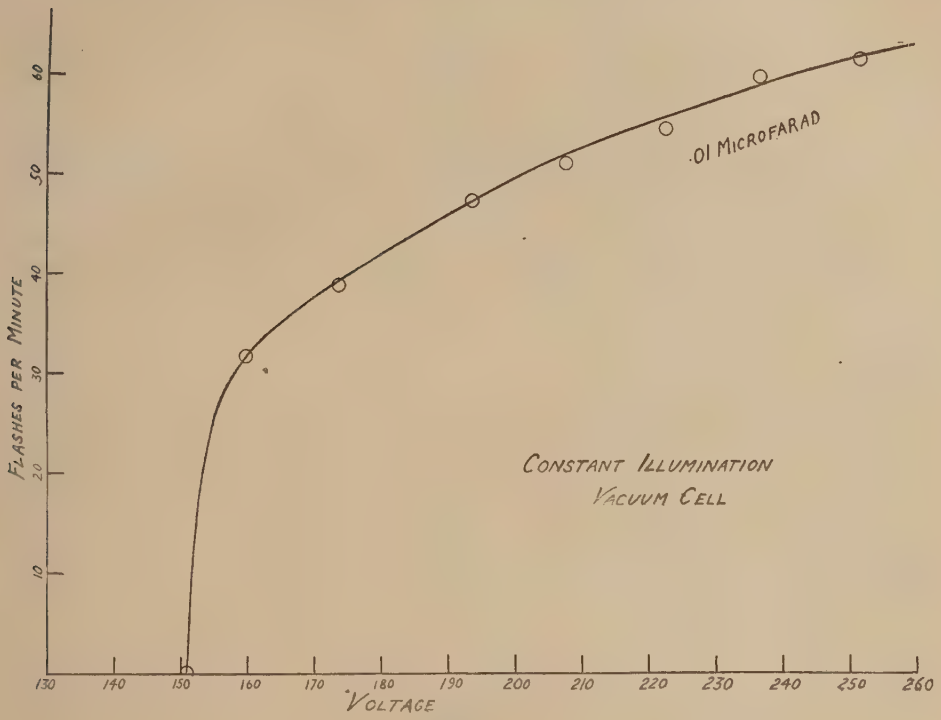
K	a	b
·00055	.43	6·02
·002	1·00	14·0
·01	3·25	45·5
·05	13·9	195·0

NOTE.—The values of b only refer to the special sodium cell used.

In order to investigate how the sensitivity varies with the voltage of the battery, a set of readings were taken with constant illumination and gradually diminishing voltage. The results have been plotted in the accompanying diagram. It will be seen that the number of flashes per minute decreases steadily with the voltage, but that at the higher voltages the slope of the curve is not so steep, so that for these values slight alterations in the E.M.F. of the high tension battery will not introduce any serious errors. It was found that the decrease in the number of flashes was simply due to the fall in charging current, as the current divided by the number of flashes remained constant, independent of the voltage down to 160 volts. Below this value the flashing became decidedly irregular, finally ceasing entirely at about 150 volts.

To measure artificial illumination or very weak daylight, it would probably be necessary to use a gas-filled photo-electric cell. The behaviour of the arrangement using a Kunz potassium cell has accordingly been investigated. These cells are not at all so satisfactory as the vacuum type cells, as their sensitivity varies very rapidly with voltage and also depends on the past history of the

cell. They are, however, much more sensitive, especially for high voltages. It was found that the number of flashes per minute in the neon lamp was also in this case proportional to the current through the cell. Table III shows a



GRAPH 3.

TABLE III.

Light in metre candles . . .	19·0	23·5	29·5	39	53	76	119	211
Current in 10^{-9} amps. . . .	10	13	17·5	23	30	44	63	111
Flashes per minute . . .	10·3	14·2	18·0	22·4	28·2	40·5	62·4	109
Light ÷ Current	1·90	1·81	1·68	1·69	1·76	1·73	1·87	1·90
Current ÷ flashes per minute . .	·97	·92	·97	1·02	1·06	1·08	1·01	1·02

Shunting capacity = ·002 microfarad. Voltage of battery = 264.

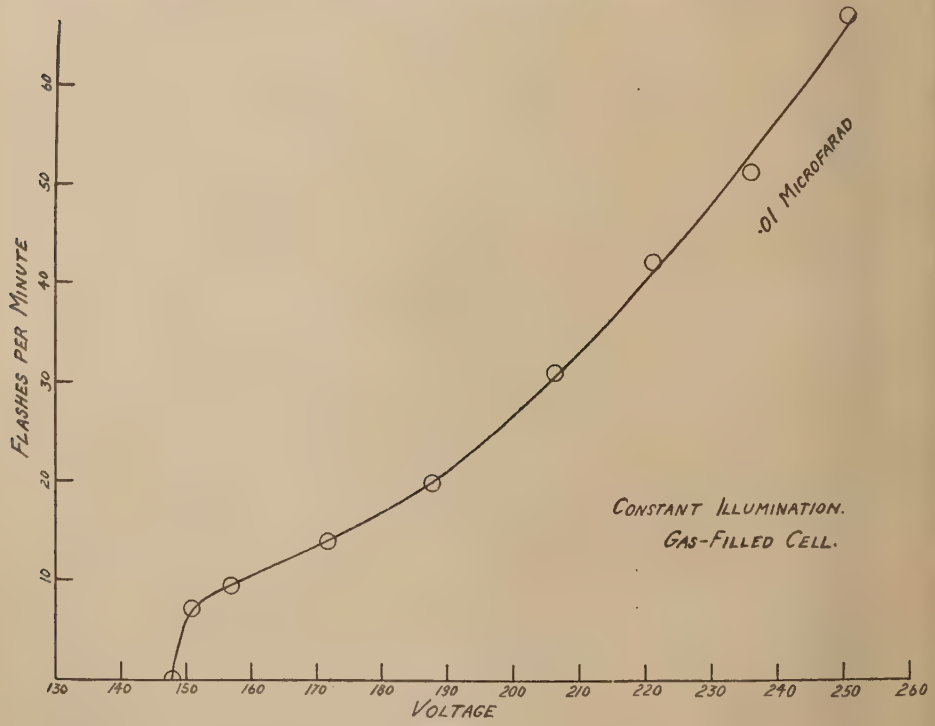
set of typical results, and Table IV gives the constants of the arrangement when used with this cell. It will be observed that for the voltage employed the Kunz cell is nearly eight times as sensitive as the sodium vacuum cell.

TABLE IV.

K	*a*	*b*
·00055	·42	·78
·002	1·00	1·85
·01	3·38	6·25
·05	13·9	25·7

K, *a*, and *b* have the same significance as in Table II.

Finally the last graph illustrates the effect of change of voltage of the battery on the sensitivity. The curve shows very plainly the difficulty of using such a cell for accurate photometric work, as the current for constant illumination varies so rapidly with the voltage. Furthermore, the slope of the curve in-



GRAPH 4.

creases with rise of voltage, so that we cannot hope to improve matters by using a higher voltage, and if we were to work at about 180 volts where the curve is not so steep, then we very largely lose the advantage of the extra sensitivity of the cell.

In conclusion, it would seem that this form of photometer would be quite useful in all cases where it was not convenient, or perhaps even feasible, to use a galvanometer or electrometer. The photometer is light, comparatively cheap, and as it contains no moving parts, it may be used in conditions which would render the use of a galvanometer impossible. It is as sensitive as a good moving coil galvanometer, but in its present form cannot, of course, compete with an electrometer. This renders it unsuitable for measuring ultra-violet light with the aid, say, of a cadmium cell, but it is possible that with a special type of discharge tube and valve amplification a similar method of measuring U.V. light could be developed. Such a photometer is rather wanting at the present day in connexion with radio-therapy.

No. 4.

INFLUENCE OF TEMPERATURE ON RESPONSE TO ELECTRICAL STIMULATION.

By HENRY H. DIXON, Sc.D., F.R.S.,

University Professor of Botany, Trinity College, Dublin,

AND

T. A. BENNET-CLARK, M.A.,

Assistant to the University Professor of Botany, Trinity College, Dublin.

[Read March 27. Published separately August 3, 1928.]

Electrical stimulation of a tissue leads to a change in its resistance. The magnitude of this response and the intensity and the energy-content of the stimulus may be accurately ascertained. Hence, as has been already pointed out (2), this type of response is particularly suited to the study of the relation existing between the magnitude of the response and the intensity and energy of the stimulus.

It is generally assumed that the resistance of a tissue is principally due to the opposition of the protoplasmic membranes to the passage of ions of electrolytes from cell to cell. An alternative explanation of the high resistance of living tissues has, however, been proposed. According to this, it is supposed that the electrolytes of the cell are held in "molecular association" with the colloids, and that such a system, apart from the resistance of the protoplasmic membranes, would have a high electrical resistance. Changes in the cell might set free the electrolytes to a greater or less extent, and so restore to them their power of conducting a current.

The work of Höber appears to dispose of this suggestion. According to him (3 and 4), the electrolytes of an uninjured cell are free, and confer on it an "inner conductivity." His first method of investigation (3) is based on the fact that the capacity of a condenser is increased if a conducting layer is introduced between the plates of the condenser, and that the increase of the capacity is, *ceteris paribus*, greater, the greater the specific conductivity of the layer. Thus, two metal plates fixed opposite to one another in a vessel containing water have a certain capacity. If now a thin-walled test-tube containing salt solutions of various concentrations is introduced between the plates,

it will be found that the capacity of the condenser increases with the specific conductivity of the contents of the test-tube. Thus, the capacity becomes a measure of the "internal conductivity." Further, it is evident that if the test-tube is filled with a mass of cells such as blood corpuscles, a comparison of the "internal conductivity" of those cells with that of the various solutions may be made. Working in this manner, Höber found that the "internal conductivity" of the blood corpuscles is closer to that of a 0·1 normal KCl solution than to that of a 0·01 normal KCl solution.

Höber also demonstrated that the subdivision of the conductivity liquid by a number of dielectric membranes into numerous compartments does not alter its effect on the capacity. This he proved by showing that the capacity did not alter when the protoplasmic membranes of the cells were made completely permeable by the addition of saponin. It is interesting to note that in this case the conductivity of the suspension taken as a whole was increased twenty times.

The "internal conductivity" of the sap in the vacuoles of cells was further demonstrated by a second method (4). Electric oscillations in a circuit comprising a condenser and a solenoid are damped if a vessel containing a solution of an electrolyte is introduced into the solenoid, because work is done in inducing currents in the electrolyte. Just as in the previous method, Höber found that blood corpuscles acted like an electrolytic solution, and damped the oscillations. Comparison showed that the "internal conductivity" before and immediately after the addition of saponin was closely equivalent to the conductivity of a 0·4 % NaCl solution. While the total conductivity before addition of saponin (*i.e.*, as long as the protoplasmic membranes were sensibly impermeable) was equal to that of 0·02 % NaCl solution, the total conductivity after the protoplasmic membranes were rendered permeable by saponin was equal to that of a 0·2 % NaCl solution.

These observations leave little doubt that there are electrolytes in the vacuoles of the cells in a condition to conduct a current, and thus the suggestion that their "molecular association" with cell colloids accounts for the high resistance of cells and tissues is rendered superfluous and improbable.

The great rise (often 50 times) in the conductivity of a tissue on addition of saponin, or on the killing of the tissue, is associated with the great increase of permeability of the protoplasmic membranes. Our experiments show that there is a continuous change of conductivity with a continuous increase in stimulation, until the stimulation becomes lethal, hence it seems unwarranted to suppose that the rise due to smaller stimuli is different in kind from the rise observed with lethal stimuli.

Similar conclusions are arrived at by M'Clendon and his co-workers (6), using a special high-frequency Wheatstone bridge. They measured the impedances of blood cells and of muscle at frequencies between 200 cycles and 1,500,000 cycles.

The impedance at 1,500,000 cycles is probably equal to the resistance of the solution inside the cell, since it does not alter appreciably when the cells are

laked; whereas the impedance at 1,000 cycles decreases considerably on laking. The following table illustrates some of M'Clendon's results:—

Table.

Frequency.	Specific Impedance in ohms.	
	Before laking.	After laking.
1,000 ...	1884·0	535·2
1,500,000 ...	322·0	322·0

In an earlier paper M'Clendon (5) showed that the impedance of a centimetre cube of blood cells at various frequencies could most nearly be imitated by a leaky capacity (of 1,500 micromicrofarads) in series with a resistance representing the resistance of the cell interiors (of 400 ohms); the leak in the capacity being represented by a resistance of 1,600 ohms in parallel with it.

It is thus safe to conclude that the changes in conductivity of a tissue on stimulation are due to changes in permeability of the plasmatic membranes of the cells. Such a change of permeability underlies the responses of tissues which constitute all tropisms. Hence, by observing resistance-changes we can observe a process which is fundamental to large categories of responses.

An additional attraction to this method is that in it the response of the actual cells stimulated is observed, and the unknown effects of conduction and of relaying in intermediate cells are eliminated. For example: in phototropic and geotropic curvatures it is quite uncertain how far the energy received by the percipient cells is absorbed or reinforced by the conducting cells. Hence, any relation which is traced between the magnitude of the response and the intensity and energy of the stimulus may in reality be due to compensating effects occurring in the cells of the transmitting tissues.

The method adopted by us has already been described. In the present investigation an improvement for graduating the duration of the stimulus was adopted. This was effected by a mechanism similar to that described by Parkinson (7). The mechanism consists essentially of a gramophone motor. On the rotating disc, and movable round a certain pivot, two metal arms are fixed. The levels of these arms are so adjusted that when the disc rotates the arms successively meet two metal hinged keys, which are fixed on the motor box close to the rim of the disc. These keys are separated from one another by an arc of about 45°. The disc of the gramophone is connected to one pole of the supply, and the first arm is in electrical connection with it. When this arm comes into contact with the first key, the stimulating current passes through the tissue, and at the same time the motion of this key actuates a relay, which makes a second path for this current. This path is available even after the arm has been carried past the first key. At some subsequent arranged time the

second arm, which is insulated from the disc, strikes the second key, and breaks the circuit of the stimulating current at another point.

It is evident that by suitable adjustment of the positions of the movable arms the duration of the stimulating current may be altered at will. In our apparatus the circumference of the disc is divided into 500 parts; the disc takes 5 seconds to perform a complete revolution, so that it is easy to arrange durations as short as one-hundredth of a second, and of any greater length.

Another slight modification of our apparatus enabled us to increase greatly the number of observations made in one day. This was effected by increasing the size of the thermostat bath, so that it contained nine test-tubes instead of two. In each of these test-tubes two leaf-squares were arranged, as in the earlier apparatus, and by a pair of dial-switches, each of these leaf-squares could be successively submitted to stimulation. This improvement suggested itself when it was realised that at certain times of the year seasonal changes in

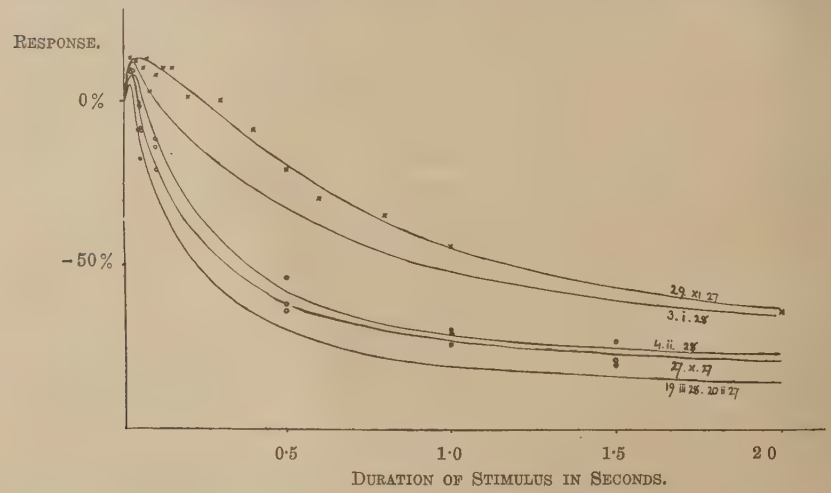


Fig. 1. — Responses at different seasons to stimuli of 150 volts at 30° C. x indicates the individual measurements determining the uppermost curve. The individual determinations for the October curve are marked o.

resistance and sensitivity are so rapid as to make observations in successive weeks not comparable. The leaf-tissues of *Hedera helix* were the subject of these experiments.

An idea of these seasonal variations of sensitivity may be obtained by inspecting fig. 1. Here the magnitude of the response measured by the percentage change of the resistance is plotted on vertical ordinates, and the durations of the stimuli—all of which had an intensity of 150 volts, 50 cycles, A.C.—are abscissae. The points defining each of the five curves shown were obtained from observations made on the recorded dates. All the squares

experimented with had been maintained at 30° C. during the experiments and for several hours previously.

It seemed possible that the different conditions indicated by these very different responses might have been due directly to the temperature conditions obtaining before the leaves were gathered. With the object of testing this surmise, separate series of leaves were kept at 3° C. for one or two days, and at 30° C. for the same time, and their behaviour during stimulation compared. As before, the squares cut from these leaves were kept at 30° C. during the experiment and for several hours before stimulation. The results, which are recorded in fig. 2, are somewhat erratic owing to the peculiar condition in which the leaves appear to be during part of the winter; but, neglecting this irregularity, there seems no evidence in this series of experiments that the seasonal change of sensitivity can be markedly modified by the temperature obtaining at the time of gathering.

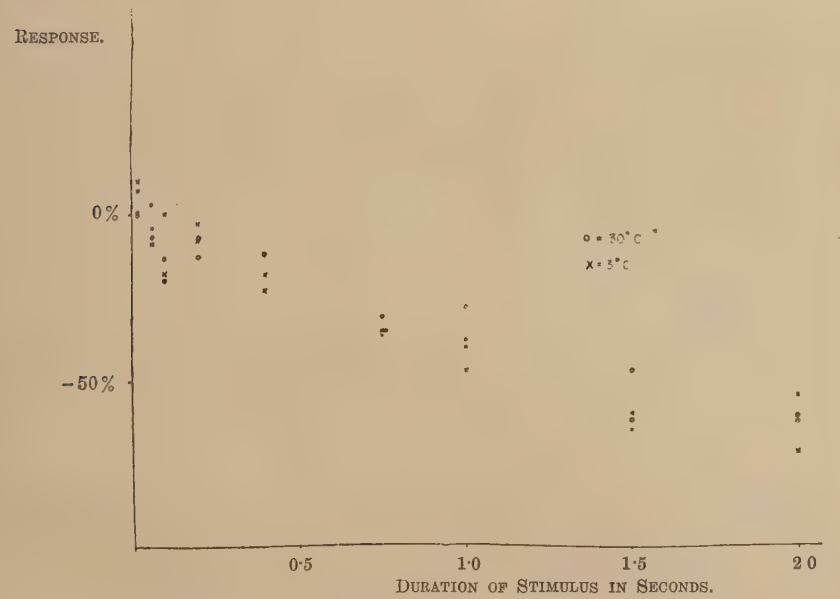


Fig. 2.—Responses of leaf-squares from leaves which had been previously kept at 3° and 30° C. to stimuli of 150 volts at 30° C. 10, 11/1/'28.

In the same way, the light conditions previous to gathering do not seem to produce any important effect on the sensitivity. This is clear from fig. 3, in which the behaviour of leaf-squares taken from branches kept in continuous darkness for five days was compared with that of those exposed to normal conditions of night and day, the leaves being, otherwise, under similar conditions. The observations were made at 30° C.

The temperature of the tissue when stimulated, however, has a very profound effect upon the response. This point is illustrated by the results embodied in figs.

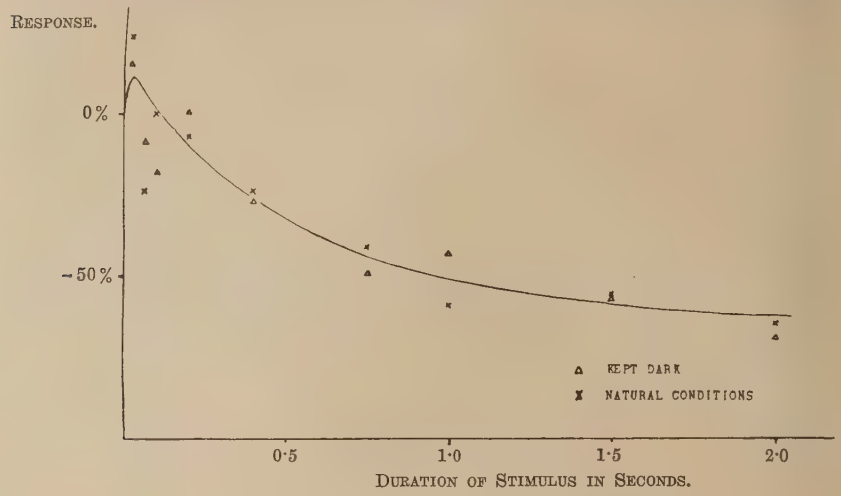


FIG. 3. — Responses to stimuli of 150 volts at 30° C. of squares from leaves which had been exposed to different conditions of lighting. 5–11/1/'28.

4, 5, and 6. In the first, fig. 4, the stimulating current had an e.m.f. of 150 volts, and in figs. 5 and 6 its voltage was 200. As before, the responses are measured as

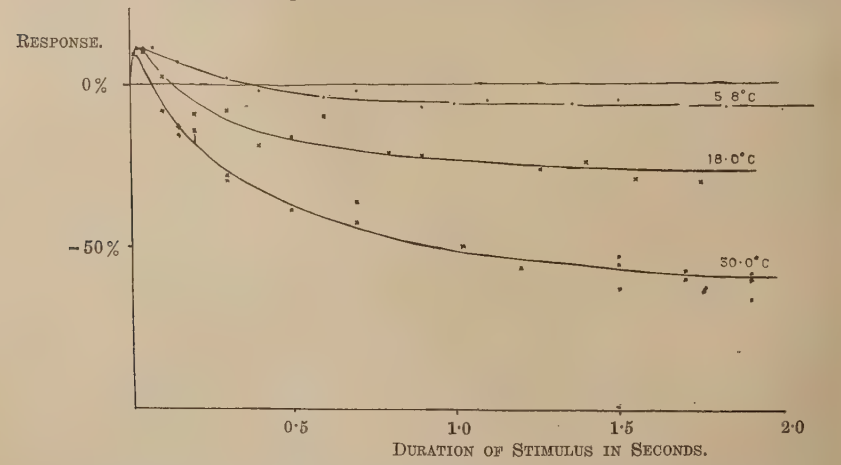


FIG. 4.—Responses to stimuli of 150 volts at various temperatures. Some points on the 30° C. curve have been omitted for the sake of clearness. 17/12/'27–4/1/'28.

a percentage change of the original resistance, and are plotted as ordinates. A rise in resistance is shown as a vertical distance above the line marking no

change, and a fall in resistance by a vertical distance below that line. In figs. 4 and 5 the points fixing each curve were obtained by experiments carried out at the temperature marked on the curve. The abscissae record the durations of the stimuli.

Fig. 6 is another way of plotting the observations shown in fig. 5. Here the temperatures of the stimulated tissue form the abscissae. The curves show how markedly the temperature may modify the magnitude of the response to stimuli having the same intensity and duration. To take an example: a stimulus of 200 volts acting for 0·02 sec. at 20° C. evokes a positive response of 20 %, while the same stimulus acting at 40° C. evokes a negative response of about

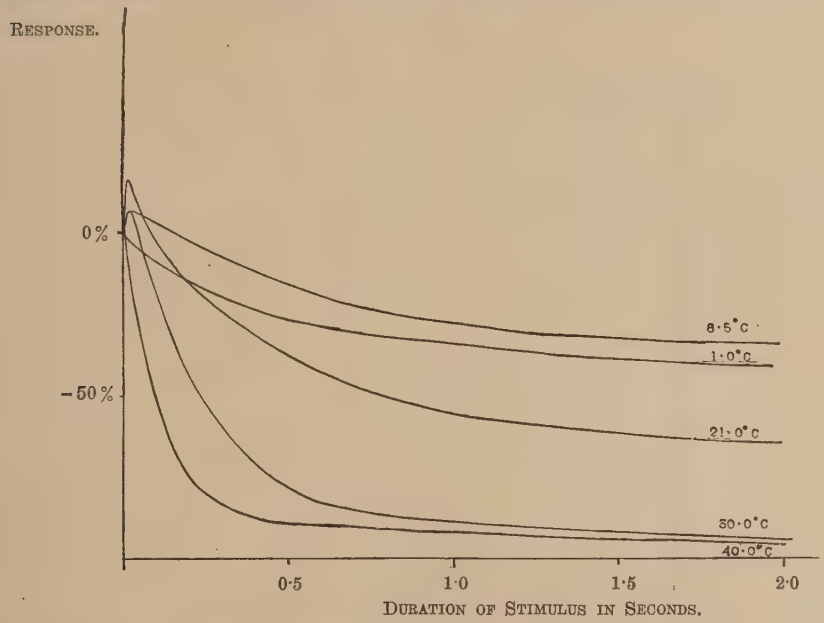


FIG. 5.—Responses to stimuli of 200 volts at various temperatures. 28/11–10/12/'27.

15 %. Thus, the sign and value of the response may be completely controlled by the temperature.

Fig. 7 shows the relation found during the month of December between the resistances of pieces of leaf, 1 cm. square, and the temperature. Each point on the curve is the average of 18 determinations. It is to be noted that the change of resistance with temperature is of the nature of a continuous fall, starting at infinity at – 5°, when the tissues are frozen, falling to 20 megohms at 0° (unfrozen tissues), 1 megohm at 2°, and, at higher temperatures, falling more and more slowly. Similar temperature-resistance curves were obtained previously, experimenting on the same leaf-square throughout the range, for

leaves of Syringa and Hedera (1). At the temperature of 50° and upwards the resistance never assumes a steady value, but continually decreases with time, until the resistance characteristic of a dead and completely permeable tissue is attained. This may be a true fall in resistance; or the observed fall in resistance may be regarded as the response to unavoidable internal and external stimuli acting on the cells whose sensitivity has been greatly enhanced by the high

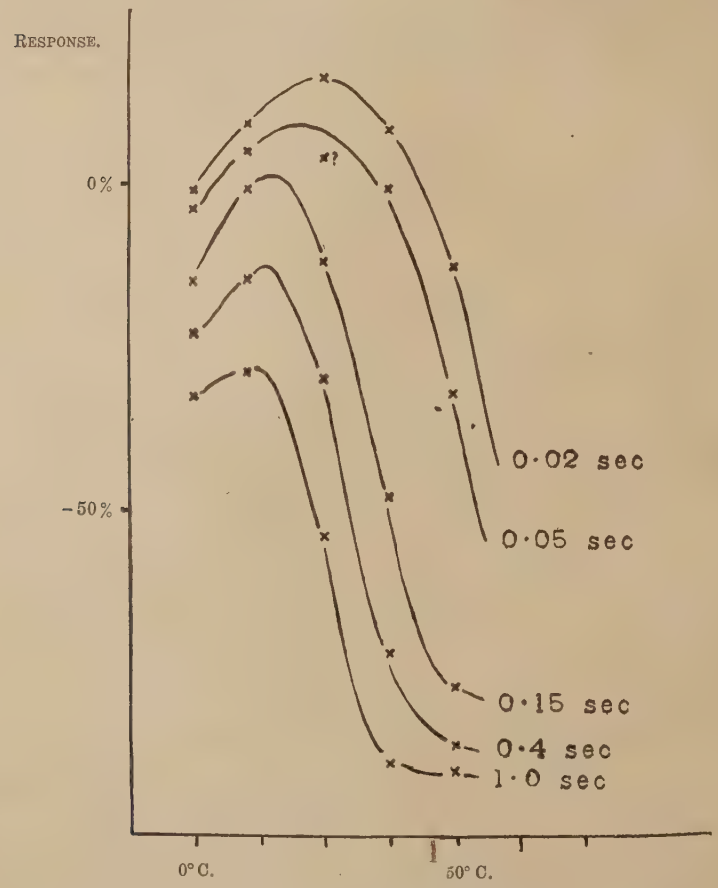


Fig. 6.—Relation between response to stimuli of 200 volts for various durations and temperature. 28/11–10/12/'27.

temperature. According to this view, if these accidental stimuli could be eliminated there would be no marked fall in resistance from 50° upwards.

The significance of these very different resistances of tissues at different temperatures will be referred to again later. One practical effect which they have

may be mentioned here, viz.: stimuli at low temperatures have a considerably smaller energy-content than stimuli having the same voltage and the same duration at higher temperatures.

That these different energy-contents of the stimulus are the principal cause of the different responses at different temperatures is negatived by various considerations.

Series of leaves were kept in darkness at 3° C. and at 30° C., and others were left under natural conditions. At various intervals the resistances and responses of these samples were examined at the temperature of 30° C. The

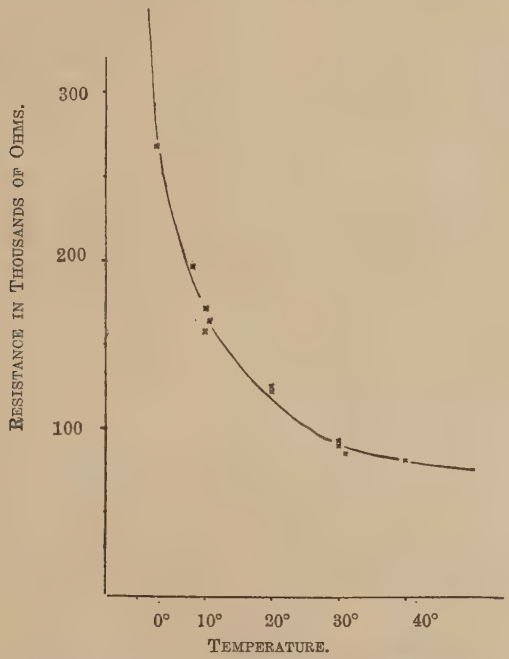


FIG. 7.—Relation between the resistance of leaf-tissues and temperature. Each point is the average of 18 determinations. 28/11–10/12/'27.

responses of all these series were identical within the limits of experimental error. The resistances were, however, very different, as the following table shows:—

Resistance in ohms (average of 18 observations).

Natural condition.	1 day dark at 3°.	2 days dark at 3°.	1 day dark at 30°.	2 days dark at 30°.
158,000	{ 170,000 / 154,000 }	134,000	90,000	94,000

Stimuli of the same voltage and duration, but of different energy-content, are seen, therefore, to evoke the same response.

To all appearance the sensitivity of the tissue is increased to exactly the same extent as its resistance has been raised by cold, or by the various other conditions which tend to lower its conductivity.

To explain this surprising result, which has been repeatedly confirmed, we may assume that in those cases where a tissue has a relatively low resistance a fraction only of the energy of the current passing is absorbed by the protoplasmic membranes. Presumably, only energy absorbed by the membranes is available for stimulation. Hence, where the resistance is low, the effective stimulus has, other things being equal, a small energy-content, although the total energy supplied to the leaf-square is high. If the resistance is high, nearly all the energy is absorbed by the membranes, and this acts as a large stimulus.

A stimulus which produces a large response is somewhat complex, since, owing to the fall of resistance, the rate of energy supply to the leaf is continuously increasing, and the fraction absorbed by the membranes is continuously diminishing, during the passage of the stimulating current.

An estimate of the extent to which the resistance may fall and the energy supplied per second may rise during the stimulus was obtained as follows:— A shunted galvanometer was placed in series with the tissue, and the alternating current in the galvanometer circuit was rectified by a crystal, so that the throw of the galvanometer was proportional to the average current passed through the tissue for a given brief duration of stimulation. The throw of the galvanometer is thus inversely proportional to the resistance of the tissue. By repeating the experiment with a known resistance in place of the tissue, the resistance of the latter can evidently be found.

The following table shows the average resistances of pieces of tissue during stimuli of different magnitudes, and also the final resistance—*i.e.*, the lowest values attained before recovery commenced. The initial resistance is taken as 100,000 ohms. These results were obtained in late March:—

Average resistance during stimulation.	Voltage.	Duration in secs.	Final resistance.
54,000	50	0·7	23,000
100,000	60	0·2	88,000

From the upper series it is clear, then, that the total energy supplied in the stimulus, where the response is large, is not given by the relation:

$$\text{Rate of Energy Supply} = \frac{(\text{Virtual Voltage})^2}{\text{Resistance at Commencement}}$$

as was assumed in our former paper. As a matter of fact, the amounts of energy supplied when the stimuli were large were considerably greater than those indicated by the formula. As, however, only the fraction absorbed by the protoplasmic membranes acts as a stimulus, and as this fraction continually diminishes as the resistance diminishes in response to the stimulating current, these two effects tend to cancel each other. Where the responses are small

(*e.g.*, 20 % and less), and the time of stimulation is short, this uncertainty as to the value of the stimulus is not of importance.

Fig. 8 shows the energy required to evoke a response of – 15 % at different temperatures. The rapid rise in the amount required between 0° and 10° C. is probably largely due to the rapid rise in conductivity (permeability) between these temperatures (see fig. 7), reducing the amount of energy absorbed by the membranes. The fall in the amount of energy required to evoke the same response over the higher range is probably to be referred to the increasing

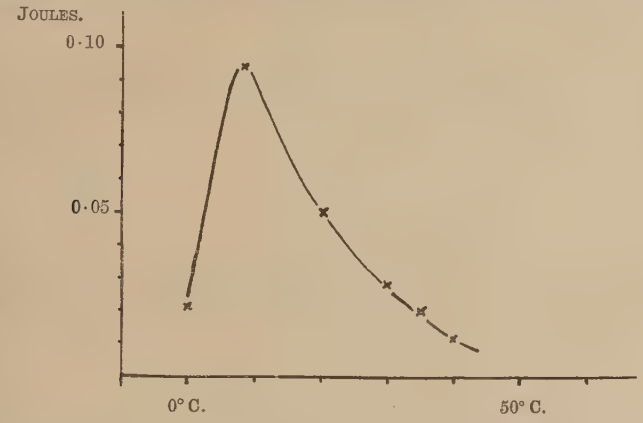


FIG. 8. — Energy of a stimulus of 200 volts required to evoke a response of – 15 % at different temperatures. 28/11–10/12/'27.

instability of the semi-permeable membranes at higher temperatures, which naturally enhances the effect of the energy absorbed. The differential effect of the rising temperature on the positive and negative responses must also have a modifying action on this curve.

SUMMARY.

1. The evidence is discussed on which is based the belief that the electrical conductivity of a tissue is largely due to the permeability of the protoplasmic membranes of the component cells to ions, and that a change in conductivity is due to, and proportional to, a change in the permeability of the protoplasts.

2. A further study is described of the effects on the permeability (conductivity) of passing alternating currents through tissues.

3. It is shown that between November and March the sensitivity of the leaf of *Hedera helix* to electric stimuli varies regularly over a very wide range (see fig. 1).

4. It is shown that temperature exerts a much more marked effect on the magnitude of a response to a given stimulus than had been previously supposed (see figs. 4, 5, and 6). The effect is possibly rendered complex by the relative independence of the positive and negative responses. At temperatures between 20° and 35° C. a change of 1° may alter the magnitude of the response as much as 10 %.

5. The effect of temperature on the conductivity is described (fig. 7), and the question of the relation between the energy supplied to the tissue and the magnitude of the response (fig. 8) is briefly discussed.

The writers wish to express their indebtedness to Dr. H. H. Poole for the help he afforded them in discussing many of the electrical questions raised in this paper.

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No. 5.

SALPINGIUM PALINORSUM: A NEW CARBONIFEROUS CORAL.

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(Plates 1 and 2.)

[Read June 26. Published separately July 23, 1928.]

This paper gives an account of a coral of unusual structure from the Carboniferous rocks of Hook Head, Co. Wexford. It consists of a slender tube, surrounded at irregular intervals by trumpet-like expansions. The name is from σαλπίγγιον, a little trumpet, and παλίνορσος, recurring. Only three imperfect specimens and a few fragments of others were found; nevertheless it seems of sufficient interest to merit description. The specimens are much silicified, and are partly weathered out on the surface of the limestone.

Salpingium, gen. nov.

Genotype.—*S. palinorsum*, sp. nov.

Diagnosis.—A genus of corals occurring in the Lower Carboniferous resembling *Tryplasma* Lonsdale in having a tubular corallum, complete horizontal tabulae, and rudimentary septa often engulfed in stereoplasm. Like some species of *Tryplasma*, the calyx widens suddenly trumpetwise, but, unlike that genus, a series of trumpets is formed, irregularly spaced, with the tube of one springing from the mouth of the preceding.

Salpingium palinorsum, sp. nov.

Holotype.—A specimen, T 153/1007, in the Geological Museum of Trinity College, Dublin (Pl. 1, figs. 1–4). A paratype has been deposited in the British Museum, R 26071 (Pl. 1, fig. 5).

Locality.—Loc. 17 w, immediately south of Doornoge Bay, and 250 yards north of the lighthouse, Hook Head, Co. Wexford.

Horizon.—Lower Carboniferous, equivalent to the C_1 sub-zone of Vaughan, about 150 to 200 feet above a dolomite band, which I correlate with the "*laminosa* dolomite" of the S.W. province of England.

Diagnosis.—As for the genus.

Description.—The corallum consists of a cylindrical tube averaging 3·5 mm. in diameter, more or less straight, flexuous, or bent, surrounded at irregular

intervals by trumpet-like expansions, or cups. As far as the evidence goes the species appears to have been solitary. The proximal end is unknown.

The outer surface is for the most part smooth, but in places subdued longitudinal ridges may be made out.

There is great irregularity in the distribution of the cups. In the length of 1 cm. several may occur, or 4 to 5 cms. may intervene between two successive cups. Each cup consists of a lamella continuous with the wall of the tube and curving outwards from it. In many cases a sharp upward bend in the lamina can be seen some distance out from the tube, which causes the former to become nearly parallel to the latter, and recalls the upright rim usually present on a tinware funnel.

On the inner surface of the cup there may be very slight but distinct septal ridges, which, in the lowest cup in fig. 6 of Pl. 1 (and Pl. 2, fig. 5), are nearly 1 mm. apart at the outer edge. A transverse section of another specimen shows much stronger ridges near the base of a cup (Pl. 2, figs. 1, 2). Other sections of cups have no trace of septa.

Just below a cup the diameter of the main tube gradually increases, so that its outer surface passes insensibly into that of the cup. Immediately above the attachment line of the cup the tube begins to contract again. The line of attachment may be transverse, or oblique. In the latter case, a transverse section will show the cup free on one side only, and fusing with the tube before the opposite side is reached. The cups may reach an extreme degree of thinness, and are sometimes seen to split into two or more laminae (Pl. 1, fig. 2). It is impossible, however, to trace them far owing to their broken condition.

Between two successive expansions the tube generally shows slight swellings topped by sharp rims, such as would be left if cups had been broken off. These (Pl. 1, figs. 5, 6; Pl. 2, fig. 7) may represent abortive attempts at cup-formation, but more likely are the scars of more delicate cups destroyed before burial.

The wall of the tube is very thick, averaging 0·5 mm. Owing to silification it presents, in thin section, a mottled appearance, which makes it difficult to say how much of what is seen may be original structure. In some cases the inner part of the wall has escaped alteration, and exhibits the characteristic appearance of stereoplasm, with a fibrous structure parallel to its surface, the fibres extinguishing straight between crossed nicols.

The inner surface of this stereoplasmic layer is smooth, or else shows in transverse section either regularly-spaced, low, wide, rounded swellings separated by sharp notches (Pl. 1, fig. 4), or, sometimes, more prominent narrow processes with rounded notches between (Pl. 2, fig. 3). I have not been able to ascertain convincingly whether these prominences are always continuous ridges, as in the cup of Pl. 2, fig. 5, or sometimes may be rows of spines. In none of the transverse sections examined are they continued all round; the succession is always interrupted by a smooth space or a defect in the specimen. If the series were completed at the observed intervals, there would be about 28.

The stereoplasm is continued on the surface of the funnels, where it gradually thins out (Pl. 1, figs. 2, 3).

The original wall outside the stereoplasm is defaced by chalcedonic replacement. Sometimes thorn-like tags, which may be septal spines, are to be made out projecting into the stereoplasm. In one longitudinal section there is a row of them (Pl. 1, fig. 3).

The tube is divided transversely by more or less horizontal tabulae, whose distance apart is often equal to the diameter of the tube but varies down to half that distance. They are mostly complete and very thin, but some show splitting, and certain of them are more or less thickened.

All the specimens were found in one bed, loc. 17 w (see p. 39), except one, which was found about 50 feet higher, loc. 17 k.

Discussion.—The formation of successive funnels is probably to be regarded as a form of "rejuvenescence," the striking appearance being due to the rapid expansion and sudden contraction, coupled with the absence of vesicular tissue and of well developed septa. Occasional partial withdrawals of the polyp are indicated by the splitting of the cups (Pl. 1, fig. 2).

It is difficult to make any suggestion regarding the systematic position of this coral. It resembles the Silurian species *Tryplasma flexuosum* (Linn.)[1] in its narrow tube with greatly thickened wall, well-spaced complete tabulae, and rudimentary septa, but differs in the possession of cups, and probably in being solitary. *Tryplasma liliiformis* R. Eth., Jnr,[2] has wide, bell-mouthed calices, and is solitary, but the calicular expansions are not recurrent.

Successions of expansions like those of *Salpingium* seem to be very uncommon. Something of the sort occurs in "*Madrepora*" *stellaris* Linn.,[3] described and figured by Weissermel[4] under the name *Endophyllum contortiseptatum* Dybowski. It is, however, a compound form with well-developed septa. Each corallite consists of a succession of segments, with their upper free margins projecting and encircling the next following segments. These expansions, in the variety *praecursor*, run out into wide thin lamellae, on which septa appear as broad flat striae.

Recurrent cups are found, too, in "*Madrepora*" *organum* Linn.,[5] which is also a compound form.

I would not, however, suggest relationship to any of the forms just mentioned.

In conclusion, I desire to thank Dr. W. D. Lang and Dr. Stanley Smith for their kind and very helpful criticism, and for drawing my attention to the other cup-bearing corals mentioned above.

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[1] Lang and Smith, Quart. Journ. Geol. Soc., 1927, p. 461.
[2] Mem. Geol. Surv. N.S. Wales, Palæontology, No. 13, pt. 2, p. 95.
[3] C. Linnæus, Amœnitates Academicae, Leyden, 1749, p. 198, and plate facing p. 312, fig. 11.
[4] Zeit. Deutsch. Geol. Gesell., vol. xlvi, 1894, p. 601.
[5] *Loc. cit.*, p. 199, fig. 6.

EXPLANATION OF PLATES.

Reference numbers, unless otherwise stated, are those of specimens in the Geological Museum of Trinity College, Dublin.

Plate 1.

Salpingium palinorsum, sp. nov. All specimens from Hook Head, loc. 17 w (see p. 39).

1–4. Holotype, T 153/1007.

1. Whole specimen, × 0·75.
2. Longitudinal section showing "splitting" of cups, × 3·5.
3. A portion of the same section further enlarged to show prominences (septal spines?), × 10.
4. Camera lucida drawing of transverse section, × 2.

5. Specimen deposited in British Museum, R. 26071, × 0·75.

6. A specimen having septal ridges in lowest cup (see Pl. 2, fig. 5), F 155/1007, × 0·75.

Plate 2.

Salpingium palinorsum, sp. nov. All specimens, except fig. 7, from Hook Head, loc. 17 w (see p. 39).

1–4. Transverse sections of specimen F 156/1007.

1. Section near base of a cup showing septa, × 10.
2. Camera lucida drawing of the same section showing further structure only visible by reflected light, × 2.
3. Camera lucida drawing of another section, × 2.
4. Photograph of the same section, × 3·5.

5. Photograph of the lowest cup in the specimen, Pl. 1, fig. 6, to show the septal ridges, × 2·5.

6. Camera lucida drawing of a longitudinal section, specimen F 157/1007, × 2.

7. Camera lucida drawing of longitudinal section of a specimen, F 158/1007 from loc. 17 k (50 feet above 17 w), × 2.

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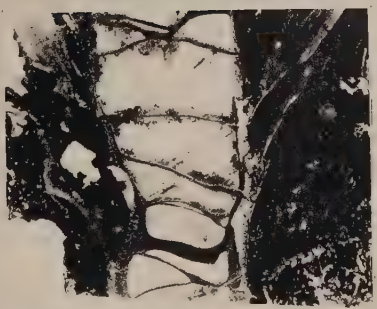

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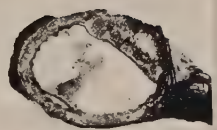

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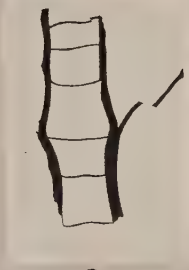

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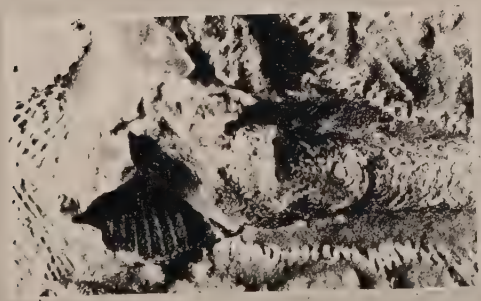

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No. 6.

REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1927.

The quantity of emanation issued during the year was 14,306 mc., as compared with 13,480 mc. in 1926, and 14,401 mc. in 1925. Detailed reports of the results of radium treatment which have been submitted by two of the largest users of emanation are printed below.

REPORT OF FORTY-FIVE CASES TREATED WITH RADIUM DURING THE YEAR 1927.

By Maurice R. J. Hayes, F.R.C.S.I.

[Read June 26. Published separately August 21, 1928.]

The total number of cases treated during the year 1927 was forty-five, which comprised the following groups:—Rodent ulcers, 20; miscellaneous malignancies, 20; non-malignant, 5.

The technique employed does not differ materially from that described in my previous reports. One may not dogmatize from the somewhat meagre success of one case, nevertheless the manifest improvement which followed the implantation of "seeds" in a radioresistent rodent ulcer of long duration suggests that in certain types of malignancies better results may be obtained from a fractional dose given over a long period than from a large dose over a short one. There is nothing new in this observation. The method has been tried with success elsewhere, but this was my first experience of it, and I am encouraged to try it again; but it would be advisable if possible to have the 1 mc. "seeds" in gold capillaries, to cut off the beta and soft gamma radiation, as recommended by Fialla, and as used by him in the Memorial Hospital, New York.

The beneficial effect of normal saline solution in the treatment of radium and X-ray ulceration is not recognised, and I would like to direct particular attention to it. In my opinion it is by far the best application for such conditions, and I do not know its equal.

All the cases mentioned in this report were treated with the emanation supplied by the Institute of the Royal Dublin Society; and I have gratefully to express my thanks to Dr. Poole and his assistants for their unfailing courtesy, and their readiness to facilitate me at all times.

Rodent Ulcers.

Twenty cases were treated during 1927. Small superficial ulcers are given 30–40 mc.-hours per square cm., screened with 2 mm. al. Large and deep ulcers

are given 60 mc.-hours per square cm. with the same filtration. When the margins are infiltrated needles are embedded in them under local anæsthesia, either combined with or followed by surface applications, the total dose being from 60–75 mc.-hours per square cm.

Recurrences are rare with this dosage, and when they do appear the margin is the usual site, and the cause under-dosage. Sometimes country patients are so anxious to return by an evening train that an adequate dose cannot be administered in the time available, and people who live at a distance will not report periodically for inspection. If they would do so, recurrences would be very rare.

The extensive and neglected rodent requiring a preliminary excision or curettage is now rarely seen. Presumably, as patients can now be assured that the malady can be cured without operation, they are more ready to submit to a painless form of treatment, which does not necessitate detention in hospital.

Late reactions appearing from the third to the fifth week have been observed in a few cases. Such reactions pass through the regular phases of the normal reaction, which appears about the tenth day, and their occurrence has been noticed more commonly in females than males. Since these late reactions are prone to occur, an interval of six weeks should be allowed to elapse before repeating the treatment, and one should not be impelled to give a second application on the assumption that the original technique was faulty, or the dosage inadequate.

One case of rodent ulcer which subsequently became radioresistent deserves special mention:—Male, aged 42, was referred to me for radium treatment in 1922, as an alternative to enucleation of his eye, and complete excision of the lower eyelid. First treated in May, 1922, the ulcer healed, but recurred on the mucosa in July, when the ulceration again healed. A subcutaneous nodule appeared at the outer canthus in October, 1923, and despite treatment there was infiltration in the soft tissues in December, 1924, which did not yield to further applications during 1925, and in January, 1926, the eye was enucleated, and the orbit cleared. This operation was followed by further radium treatment in February and June, 1926, the estimated dosage on all occasions being 60 mc.-hours per square cm. of tissue affected.

As the ulcer was not healing, high-voltage X-rays were tried in September, 1926, with no better result. In March, 1927, five radon "seeds" (1·2 mcs. in each) were embedded round the margins of the ulcer, following which the ulcer commenced to heal. In October, 1927, five more glass capillaries, each containing 1 mc. radon, were embedded, and three months later the whole socket was almost completely covered by healthy scar tissue, but there was a large indolent area about the size of a five-shilling piece in the temporal region, into the margins of which eleven glass capillary "seeds," 1 mc. in each, were again embedded. The reaction from these had not completely disappeared when he was advised to go elsewhere for "Erlangen treatment," and he was given 1½ hours' treatment the first day, and two hours' the next day. This was followed by a violent reaction, and severe headache and trismus, and the patient could get no sleep.

He returned to me in February, when he was anæmic, and looked very ill. The headaches and trismus were still present, and he could take no solid food. The ulcer was covered by a white necrotic slough, and it was very painful; the outer bony margin of the orbit was denuded, black in colour, and necrotic, and the condition was obviously a severe X-ray burn of the third degree, which resulted from the summation effect of the radon seeds and the "Erlangen treatment," which were given at such brief intervals. One is glad to say that, with the aid of normal saline compresses, the ulcer is again showing evidence of healing.

The details of this case are recorded at such length to show: (1) the benefits derived from implanting "seeds" in a radioresistent case, and (2) the unwisdom of irradiating a case which has recently been under treatment elsewhere without full inquiry as to previous history and dosage.

Carcinoma of the Lip.

Five cases were treated. All were men, and the lesions were on the lower lip. Ulceration was present for one month, 1; two months, 1; one year, 1; four years, 1; eight years, 1. None had evidence of glandular involvement. The ulcers were small and superficial in three, and they were irradiated by surface application with 2 mm. aluminium filters, 60 mc.-hours per square cm. One large cauliflower ulcer, which had been growing rapidly, was treated by inserting five needles, the dose being 80 mc.-hours. The next day a surface application, 2 mm. al. filter, was given, 333 mc.-hours. The total irradiation given was 413 mc.-hours. The size of the lesion was about a cubic inch.

Another smaller ulcer was treated similarly.

As a routine, the whole submaxillary region is irradiated at 1·5 cm. distance, 2 mm. brass filter. It is divided into three "fields," 3 cm. × 2 cm., and the total irradiation dissipated in each field is 9 millicuries.

The ulceration has healed in all these cases, and there is no evidence of recurrence in four of them. One, however, was suffering from lymphosarcoma, of which, I believe, he has died.

Carcinoma of Tongue.

Three cases treated. One of these was recurrent nine years after partial excision of the tongue and removal of the submaxillary glands. There was a fungating fœtid ulcer in the stump, which had grown rapidly within a month. The patient's age was 78. He declined, and was not fit for operation. Two needles were embedded in the ulcer; dose, 707 mc.-hours. Three days later the submaxillary and cervical glands were treated by high-voltage X-rays (·09 A.U., F.S.D., 30; F., 12 × 10; ·5 zn. plus 2 mm. al.; 55 minutes. One field each side of neck, including submaxillary region).

The caustic effect of the radium, as expected, was manifest within a fortnight, when a lemon-coloured adherent slough formed. This separated quickly by syringing with normal saline solution, and packing the ulcer crater with cotton wool soaked in the saline. The pain was readily controlled by aspirin. The

ulceration was completely healed within six weeks. His doctor recently reported that this patient is quite well. The writer knows of nothing to surpass the frequent application of normal saline solution in promoting the rapid healing of radium and X-ray ulceration. It is almost magical in its action.

One early case, and one which was advanced and inoperable, and growing rapidly, were treated by the local implantation of needles. The estimated dose in each case was 60 mc.-hours per cubic cm. of tissue involved. The glandular area in each case was given deep X-ray treatment with the factors as stated above.

In each case the doctors report that "the tongue is quite healed."

Carcinoma of Right Vocal Cord.

One case was treated by embedding needles under local anæsthesia without laryngotomy. Dose, 72 mc.-hours. Two days later high-voltage X-rays were applied, 100 % D.D. The symptoms were ameliorated, but the patient died from the disease four months after treatment.

Epithelioma of the Palate.

A very advanced and inoperable case, which was referred to in my previous reports. A busy merchant, engrossed in private and public affairs—he was most careless and irregular in his attendances, and he never gave the opportunity to treat him thoroughly or systematically, nevertheless he was enabled to attend to the manifold duties of his busy life for six years through the amelioration which he always got from the applications. He died during the year.

Carcinoma of Rectum.

Radon was employed to supplement high-voltage X-rays in one case. Retardation—still under observation.

Carcinoma of Uterus.

Four advanced and inoperable cases were treated. All are ameliorated. Hæmorrhage and discharge ceased, and ulceration has healed.

Cutaneous Epithelioma.

Four cases treated. Two healed. Two recently treated are healing.

Endothelioma of Nose.

Child, aged one year. Simulated a cavernous angioma, and underlying vessels were ligated without effect. Biopsy revealed endothelial cells. As the tumour was growing rapidly, the case was referred to me for treatment. A surface application of 49 mc. 2 mm. brass filter was given for 4½ hours, in June, 1927; and 46 mc. for 6 hours, in August, 1927, with the same filtration. The tumour had completely disappeared in October, leaving no cutaneous pigmentation.

This case is doing very well.

Dupuytren's Contraction.

Both hands were affected. Excision of the fibrous tissue from both palms gave no relief, and when he came for treatment the three inner fingers of both hands were flexed and immobile. A total irradiation of 800 mc.-hours: 2 mm. brass: surface: was given to each palm; four separate areas; extending over four days.

This was followed by radiant heat and massage, and three months later the patient was able to play the piano.

Warts.—Four cases were treated, and all are apparently cured. Dose, 30 mc.-hours, the surrounding area being protected with lead.

REPORT FOR THE IRISH RADIUM COMMITTEE (ROYAL DUBLIN SOCIETY) OF RADIUM WORK CARRIED OUT IN THE YEAR 1927.

By Walter C. Stevenson, M.D., B.Ch., D.P.H.,
Surgeon, Dr. Steevens' Hospital, &c.

During the year 1927 radium treatment has been administered to 247 cases—126 suffering from malignant disease, and 121 from non-malignant conditions. Of these, 188 were treated at Dr. Steevens' Hospital, and about half the remainder at other General Hospitals in Dublin. The duration of a treatment varied from a few minutes to a few weeks, and 290 treatments were given altogether.

The main source of radiant energy employed was radium emanation or radon, supplied in glass capillaries by the Irish Radium Committee of the Royal Dublin Society. The radon, which is procurable once or twice a week, is sometimes utilised for as long as two months, till the capillaries are completely exhausted. As a separate record is kept of each supply, it is possible to use the capillaries and know their strength at any time by the aid of the emanation table. Occasionally an initial supply of 200 millicuries has been kept distinct, and in use, till the activity is below 0·1 millicurie. Usually when a supply goes below 1 or 2 millicuries it is mixed with older capillaries in an applicator, useful for out-patients, and the combined strength recorded; so that the minimum amount of radiant energy is wasted as the emanation is in constant use, being transferred from one patient to another as each treatment is completed. In this way it has been possible to treat a large number of non-malignant cases by emanation when the capillaries have become too weak to be of any use for malignant cases. In a few cases bare capillaries have been implanted in malignant growths, and left there; but this is an exceptional procedure. Very weak, bare capillaries have been used by surface application

to stimulate epithelialization, and also stronger capillaries in small sinuses and in cysts to destroy the lining walls, and to effect the cure of a chronic septic condition. This technique, which is essentially beta-ray treatment, is combined with more prolonged gamma radiation. In the malignant cases particularly, 53·93 milligrams of radium element, which are contained in 6 cells, described in the 1924 Report, have been in constant use during the year—frequently in needles for insertion into tumours, sometimes collected together in one tube—for surface application in separate tubes.

In the last Report (1926) the exact dosage in practically all of 183 cases treated was given. It was pointed out that the dose depended upon the amount and distribution of the radio-active material, the dimensions of the radiating focus, the amount of screening employed, and the distance from the nearest cells at which they were used. The dosages in the year 1927 have not been materially altered, except that surface radiation has been somewhat diminished in treatment of cases about the neck, so as to produce less reaction and constitutional disturbance. As in former years, the best results have been obtained in cancer of the breast and of the body of the uterus, with the exception of malignant disease involving the skin alone, as small epitheliomas and rodent ulcers, which usually disappear after one treatment by needles combined with surface applicators. Except the last-mentioned cases, the malignant disease was far advanced in most of the patients. No patients were treated except inoperable cases, or those which had recurrence after operation. Attempt has been made to follow up some of my cases, but a number of forms have not been returned, and the information on those returned has not been illuminating. Some of the very advanced cases are known to have died since treatment. The majority have improved, at least temporarily, and a few are reported to be well. The number of cases of cancer that has been met during the year is so great that it is felt almost impossible to deal with each case adequately, and the treatment has been mostly palliative, and the patients birds of passage—a number of them coming from the country and from other Hospitals; they have, unfortunately, been lost sight of as soon as their treatment was completed. It is very exceptional for these patients not to appreciate the benefit they have derived from the treatment, and they are most grateful that something further has been done for them when they were led to believe that their cases were hopeless.

The following list shows the number of patients and the conditions treated during 1927 :—

MALIGNANT CASES, 126.

A. CANCER OF BREAST 7

B. CANCER OF UTERUS 15
Body, 1; *Cervix*, 14.

C. CANCER OF MOUTH 34
Tongue, 15; *Palate*, 4; *Tonsil*, 5; *Tonsil and Tongue*, 1; *Floor*, 6; *Fauces*, 2; *Cheek*, 1.

C.C. VARIOUS CANCERS 44
Maxillary Antrum, 2; *Nose*, 1; *Naso-Pharynx*, 1; *Pharynx*, 7; *Oesophagus*, 4; *Stomach*, 1; *Rectum*, 5; *Orbit*, 1; *Vaginal Caruncle*, 1; *Lip*, 6; *Skin*, 15.

D. SARCOMA 17
Brain, 1; *Nose*, 1; *Eye*, 1; *Max. Antrum*, 1; *Lower Jaw*, 1; *Tonsil*, 3; *Neck*, 4; *Mediastinum*, 2; *Breast*, 1; *Axilla*, 1; *Vagina*, 1.

E. RODENT ULCER 9

NON-MALIGNANT CASES, 121.

ADDISON'S DISEASE 1
ADENITIS 4
ADENOMA 1
ANGIOMA 1
CHRONIC LYMPHATIC LEUCAEMIA 1
CORNS 2
CYST 3
DEAFNESS 10
DENTAL 1
DUPUYTREN'S CONTRACTION HAND 3
FRACTURES 5
GASTRIC ULCER 1
GOITRE 1
HALLUX RIGIDUS 1
HORN 1
KELOID 2
LEUCOPLAKIA 1
LICHEN PLANUS 1
LUMBAGO 2
NAEVUS 5
NERVE INJURY 1
OSTEO-ARTHITIS 1
OTORRHOEA 2
PAPILLOMA 1
PIGMENTED SKIN 2
PYORRHOEA 1
RHEUMATISM 4
SCARS 5
SEPSIS 14
SINUS 3
SPRAIN 1
SPRING CATARRH 1
SORE TEETH 1
SORE THROAT 1
TRACHOMA 1
TUBERCULOUS CONDITIONS ... 25
Bone, 1; *Enteritis*, 1; *Pus Tubes*, 2; *Ulcer*, 1; *Joints*, 4; *Larynx*, 1; *Lungs*, 1; *Lupus*, 3; *Ulceration Nasal Mucous Membrane*, 3; *Peritonitis*, 8.
ULCERS 5
WARTS 5

The general plan of treating cases of malignant disease has been to treat the tumour and surrounding area systematically, where possible by buried tubes or needles, combined with surface radiation. As well as employing long needles, which are systematically withdrawn to radiate different parts of the tumour, tubes with silk attached have been buried by means of a trochar and cannula, a stylette being utilised to push the tubes into the required positions while the cannula is being withdrawn. The tubes are torpedo-shaped, to facilitate their removal. Hard beta rays are available for treatment with the needles. As the radon capillaries when received and radium cells have an activity of about 10 milligrams of radium element, the dose is fairly concentrated, and buried treatment does not usually last longer than 48 hours at the most. For surface radiation, also, the treatment is seldom prolonged more than a week. As in previous years, 2 cm. thickness of felt is employed as a distance piece, and as many as 50 gamma-ray tubes, each containing a radon capillary or radium cell, employed at one time, arranged in two or more applicators to obtain cross-fire, and moved about as required. The radiating area is usually 10 × 2 cm., the size of the felt of the applicator being about 5 × 12 cm. Frequently, in a position like the neck, cross-fire is obtained by an applicator 18 cm. long, which more than half encircles the neck. Although I believe that some cases would probably benefit more by surface or buried treatment of three times the period now employed, this is not always possible on account of shortage of beds, the number of patients that require treatment, the holding up of apparatus for a long period, and the inconvenience of the rapid loss of activity of radon.

There is no doubt that buried radon or radium is the most efficient way of treating malignant tumours. The case of sarcoma in the axilla treated in 1927 appears to prove that good immediate results may be obtained without burying. This patient, when admitted to Dr. Steevens' Hospital, had a fairly large tumour in the axilla, which had recurred within a very short time of its removal; he also had a big mass projecting 8 cm. from the side of his neck, which obliterated its contour. There was a smaller growth between the scapula and spine. He was practically bedridden, his right arm was œdematous, and he had considerable pain. The small skin punctures made to insert tubes in a couple of places caused so much hæmorrhage that buried treatment had to be abandoned. Surface application, with an initial dose of 250 millicuries, was used for five days over the various areas. Total dose, 163·8 millicuries disrupted. In three weeks the patient was able to go out; the tumour in the axilla had practically disappeared; nothing could be felt in the scapular region, and the contour of the neck was normal. On deep palpation in the last region, two small glands, about the size of hazel nuts, could be felt; the pain had disappeared, and most of the œdema in the arm. I suspected at the time that he probably had metastases in the lung, but, even if he had, he was not fit for further treatment then, as he had had as much radiation as he could stand. He died, I heard, six months later from an intra-thoracic growth; but the tumours which had been treated and the œdema in the arm never returned.

With regard to the radium treatment of non-malignant cases, I first used it in 1914 in a case of severe scarring and pain in the hand, which had been caught in a calendaring machine about a year previously. On account of the intense pain in the fingers, the hand was kept quite rigid, and was useless. A few days after the radium treatment by emanation buried in serum needles the patient was able to move her fingers comparatively freely, and in a couple of months' time she had quite a useful hand. About three years later I began to treat war injuries, and obtained somewhat similar results in a large number of the wounded in the Great War. For instance, pensioners with painful amputation stumps were enabled to wear their artificial limbs. Gradually, the use of radium has extended to the treatment of chronic infectious conditions—as tuberculosis, and later in chronic sepsis. The effects of radiation in tuberculous peritonitis have been most gratifying in relieving symptoms, and shortening the convalescence, and in most cases effecting a cure. I instance two of last year's cases which were referred to me after laparatomy had been performed. In one, the whole peritoneum was found to be studded with small tubercles. A month after the operation she was still vomiting, and the abdomen was distended and tender. These symptoms completely disappeared after treatment by radiation, the improvement starting within a few hours of its commencement, and in a couple of months' time the patient was apparently in good health. In the second case the posterior layer of the rectal sheath was much thickened; the omentum and intestines were bound together by adhesions, which were so severe that no attempt was made to interfere with them. This patient was radiated a week after her operation for five days, and five weeks later for a similar period, after which she was able to walk out of the Hospital, though it had originally been intended to keep her in bed for three months. About four months later she appeared to be in excellent health.

Radiation by surface application has been used in chronic infective conditions where there has been a good deal of brawny induration for one or two months, and has been followed by complete recovery. A couple of these cases very much simulated actinomycosis, though the actual fungus was not found. One case last year shows strikingly the beneficial effect of mild radiation. This patient had a compound fracture of his ankle about fifteen months before; the bones had become firmly united, but the usual œdema which follows a fracture of the lower limb was increased by the chronic inflammatory products round an ulcer of area 2 × 1 inches area, situated on the external malleolus. This ulcer was quite indolent, and had remained *in statu quo* for months, in spite of prolonged rest in bed, massage, and every form of treatment usually employed. The chief trouble about it was its extreme painfulness, which prevented the patient sleeping at night, and on account of which he had on several occasions asked to have the limb amputated. The region of the ulcer was treated by an initial dose of 5 millicuries, in 15 gamma-ray tubes, in an applicator of 2 × 7·5 area, for 24 hours, over the ulcer, and for a similar period over the four surrounding areas. The pain was relieved after a few hours, and the patient told me he had had the first good night for months. When the

treatment was completed, most of the induration had disappeared, and ulcer showed signs of healing, and he was able to move his ankle freely. When last seen, about three months later, the ulcer was represented by a slit about ¼ inch wide and 1½ inches long. He had practically full movement of his ankle-joint.

As other examples of the effects of radium treatment I may cite a case of discharge from the ear, persisting for four years after a mastoid operation, which completely cleared up about a month after treatment with a bare radon capillary containing 3 millicuries for ¾ hour, and the same capillary in a gamma-ray tube for 6 hours. Three cases of tuberculous ulceration of the nasal mucous membrane had practically healed when last seen, after one beta and gamma radiation in the nostril. A case of a bleeding point in the nose, which prevented the patient sneezing or blowing her nose, as it caused severe epistaxis. This was cured by the application of a radium emanation capillary in a piece of bicycle valve-tubing for ½ hour, although other methods of treatment had failed. Similarly, inveterate spring catarrh of the conjunctiva has yielded to repeated beta-radiation, and chronic discharging sinuses from congenital cysts and ischio-rectal abscesses after operation have healed up after combined beta and gamma radiation.

During the last couple of years I have used mild and prolonged radiation, at first very tentatively, for acute septic conditions. To put it briefly, I have found that it has acted almost like a charm in carbuncles, some of which have been very extensive. In a couple of cases, where there was already much sloughing, the dead tissue was first removed under an anæsthetic. Radiation at once relieved the pain and stiffness, hastened the healing, and the final result has been a soft and fairly inconspicuous scar.

In my limited experience of two cases of erysipelas I believe radiation is a sound method of treatment.

As an example of the effect of radiation on an acute infective condition, a patient was sent to me to have her neck opened for a large swelling, which had quickly followed a tonsillar abscess. Although the swelling was great, and very hard, there was no localizing sign of pus. I decided to wait till the morning before incising the area. I happened to have 6·8 millicuries of emanation in a 10 × 2 cm. applicator, which I applied for 8 hours during the night. The next morning the swelling had gone down slightly, and she stated that the pain was better, and that her neck was less stiff. The indications for an immediate opening were not so marked as the night before, but I was afraid to continue the radiation, and substituted an antiphlogistin poultice. That afternoon she asked me to put on the radium again, as it made her feel so much more comfortable. I concluded that radiation was not harming her, and the applicator remained on for a week, when practically all the induration and swelling had disappeared. On the tenth day a soft spot, which could be covered by a finger, could be felt; this was incised with a tenatome without an anæsthetic, and about a dram of pus evacuated. A few days later a similar puncture was made a little lower down for better drainage, and in about six weeks the whole condition

had cleared up. This patient was particularly anxious not to have an anæsthetic, and not to have a scar, and I believe there is little doubt that if I had not used radium it would have been necessary to inflict both on her. In reference to this case, I may say that it is cited more as showing the effect of radiation on acute infective condition rather than as an example of how such conditions should be treated. At the same time there are conceivable cases where an anæsthetic and operation would involve great risks, which might be obviated by this line of treatment.

In conclusion, it should be pointed out that the radium treatment of non-malignant conditions, if risks are to be avoided, and if it is to be of help in throwing a light on its action in a malignant disease, involves much care and time in carrying it out. As far as the former affections are concerned, radium treatment is of value to the patients in relieving pain, shortening convalescence, and, I believe, in certain circumstances, can turn the tide of battle in the patients' favour, and be the determining factor in saving their lives.

Finally, no account of radium work in Dublin is complete without expressing our indebtedness to Dr. Poole and his laboratory staff at the Royal Dublin Society for their courtesy, accurate measurement, and care when supplying emanation. I also wish to thank those in specialised branches of surgery who have co-operated with me in carrying out radiation treatment; and my Residents at Dr. Steevens' Hospital for their valuable help in the exacting routine work which radium radiation necessitates.

No. 7.

SPECTROGRAPHIC ANALYSES OF IRISH RING-MONEY AND OF A METALLIC ALLOY FOUND IN COMMERCIAL CALCIUM CARBIDE.

By A. G. G. LEONARD, F.R.C.Sc.I., B.Sc., Ph.D.,
AND
P. F. WHELAN, B.Sc.

[Read June 26. Published separately August 22, 1928.]

I.—Ring-money.

In 1926 an associated group of objects of great archæological interest was discovered in the neighbourhood of Abbeyfeale, Co. Limerick, and is now exhibited in the Irish Antiquities Division of the National Museum. These objects are dated by Mr. L. S. Gogan, of that institution, to the period of transition between the Bronze and Iron Ages, perhaps about 500 B.C.

Part of the find consisted of a number of penannular rings, of the type sometimes called ring-money. Specimens of ring-money are usually about one inch in diameter, and consist, sometimes of gold, sometimes of a core of base-metal, resembling copper, encased in a thin sheath of gold.

The specimens under examination appeared to be unique, as they showed a core of a white base metal where the gold casing had been displaced.

A spectrographic examination of the rings was accordingly undertaken at Mr. Gogan's request to ascertain the nature of the metals constituting the rings.

Spectrographic Analysis.

The spark spectra of cadmium and gold were photographed, using a Hilger one-prism quartz spectrograph (No. 8), and the distances of the more prominent and sharply-defined lines from a standard line (Cd 5 : λ 4799·9) were measured with a Hilger micrometer reading to 1/10,000 inch. These distances were plotted against the wave-lengths of the lines in international Ångström units, on paper ruled in tenths of an inch, on a scale of one inch to every 1/100 inch measured on the plate, and 1/10 inch to each Ångström unit of wave-length. By reference to the curve thus obtained, the wave-length of a line, whose distance from Cd 5 on the plate had been determined, could be found. Owing to the partial exposure of the base metal cores, no difficulty was experienced in passing an electric discharge between two cores.

The spark spectrum was photographed, and showed the presence of tin. A well-defined tin line being selected as standard, the lines were measured, and

by reference to the interpolation curve, the wave-lengths recorded. From wave-length tables they were then completely identified. In addition to the tin spectrum, the more persistent lines of copper and lead were detected.

The base metal forming the core of the ring is, therefore, tin in a very pure form, with traces only of copper and lead. It is interesting to note that this metallic tin was actually purer than that in a pair of "pure" tin electrodes used for comparison purposes. In this connection, Bannister has also observed a remarkable degree of purity in a metallic tin sheath, ascribed to Mediæval or possibly Roman date, on exhibit in the Shrewsbury Museum (J. Inst. Metals, **35**, 1926).

In the following table, details are recorded of the spectrographic analysis. The wave-length values are, where possible, those given by Kayser in his "Handbuch der Spectroscopie," and are in international Ångström units. Otherwise, they are taken from the determinations of Exner and Haschek, recorded in the same work. The corrections of wave-length found for the tin lines have been applied to the measurement of other lines in their vicinity. In the last three columns are recorded the wave-lengths of the lines identified, together with their intensities (I), and persistencies (P), as determined by Hartley for solutions of the elements concerned (Phil. Trans., 1884, ii).

The system devised by Pollok (Sc. Proc. R. Dub. Soc., 1907, p. 189) is employed to denote in a convenient manner the relative persistency of the lines as determined for solutions of salts of the elements.

Thus :—

ϕ denotes a line which shows in a 1 % solution.
χ " " " ·1 % "
ψ " " " ·01 % "
ω " " " ·001 % "

RING-MONEY.

Base Metal Core.

λ from curve.	Corr.	Element	λ	I.	P.
4524·6	+ 0·3	Sn	4524·90	30	
4057·2	+ 0·8	Pb	4058·00	300	χ
3802·0	− 0·7	Sn	3801·32	30	χ
3759·8	− 0·2	Cu	3759·60	2	
3687·8	− 1·1	Sn	3686·70	2	
3656·5	− 0·6	Sn	3655·91	3	
3639·9	− 0·2	Pb	3639·72	20	χ
3575·2	− 0·6	Sn	3575·80	2	
3374·0	0·0	Sn	3374·00	1	
3352·4	+ 0.1	Sn	3352·47	20	χ
3330·1	+ 0·8	Sn	3330·86	6	χ

RING-MONEY : *Base Metal Core—continued.*

λ from curve.	Corr.	Element	λ	I.	P.
3283·2	+ 0·4	Sn	3283·60	20	χ
3274·0	+ 0·1	Cu	3274·08	20	ψ
3247·4	+ 0·3	Cu	3247·66	30	ω
3175·4	− 0·3	Sn	3175·15	20	χ
3142·9	− 0·9	Sn	3142·01	5	
3033·1	+ 1·1	Sn	3034·24	50	χ
3032·3	+ 0·7	Sn	3032·99	3	χ
3008·0	+ 1·3	Sn	3009·33	50	χ
2912·9	+ 0·7	Sn	2913·65	10	
2873·8	− 0·4	Pb	2873·42	10	χ
2863·8	− 0·3	Sn	2863·52	20	ψ
2850·0	+ 0·7	Sn	2850·72	10	φ
2839·6	+ 0·6	Sn	2840·10	20	
2831·8	+ 1·3	Pb	2833·13	15	χ
2812·0	+ 1·7	Sn	2813·70	4	
2811·2	+ 1·5	Sn	2812·72	3	χ
2802·0	+ 0·1	Pb	2802·10	30	
2783·5	+ 1·6	Sn	2785·15	3	φ
2779·6	+ 0·3	Sn	2779·89	4	χ
2704·8	+ 1·8	Sn	2706·57	10	ψ
2660·1	+ 0·5	Sn	2660·60	6	φ
2657·6	+ 1·1	Sn	2658·71	10	χ
2613·3	+ 1·1	Pb	2614·29	10	χ
2593·1	+ 1·4	Sn	2594·54	3	φ
2570·0	+ 1·7	Sn	2571·70	5	χ
2544·6	+ 2·2	Sn	2546·80	3	χ
2493·1	+ 2·7	Sn	2495·81	4	φ
2482·6	+ 0·8	Sn	2483·44	4	χ
2427·7	+ 1·8	Sn	2429·56	10	ψ
2420·0	+ 1·8	Sn	2421·80	6	
2368·6	− 0·3	Sn	2368·31	3	φ
2355·4	− 0·5	Sn	2354·93	4	χ
2334·5	+ 0·4	Sn	2334·87	2	φ
2318·4	− 1·0	Sn	2317·38	3	φ
2269·2	− 0·2	Sn	2269·02	2	
2246·1	0·0	Sn	2246·11	2	φ

In order to determine the foreign metals present in the gold sheath, a photograph was taken of the core with a long slit, superimposed on a spectrum of the gold sheath with a short slit. The same tin line as before was taken as

standard, and the distances of the short lines not coincident with long lines, and of such tin lines as would assist identification, were measured.

When identified, it was seen that several silver lines and a few copper lines of great persistency were present.

The gold sheath contains, therefore, silver and a trace of copper.

Details of the measurements and identifications are given in the following table:—

RING-MONEY.

Gold Sheath.

λ from curve.	Corr.	Element	λ	I	P.
4526·4	+ 0·3	Sn			
4046·0	+ 0·4	Ag	4046·45	2	
3949·9	− 0·3	Ag	3949·62	2	
3900·0	+ 0·7	Au	3900·72	2	
3875·6	− 0·8	Au	3874·83	3	
3816·1	+ 0·3	Au	3816·40	5	
3801·4	− 0·1	Sn			
3775·8	+ 1·4	Au	3777·25	2	
3769·6	+ 0·5	Au	3770·14	4	
3762·1	+ 1·0	Au	3763·10	2	
3751·3	+ 1·6	Au	3752·90	3	
3732·1	+ 0·6	Au	3732·68	2	
3686·0	+ 0·7	Sn			
3655·5	+ 0·4	Sn			
3622·0	+ 0·9	Au	3622·93	6	
3580·4	+ 1·0	Au	3581·45	4	
3567·5	+ 0·8	Ag	3568·30	1	
3552·4	+ 0·1	Au	2552·47	6	
3451·3	+ 1·0	Au	3452·27	2	
3444·0	+ 1·6	Ag	3445·63	1	
3391·6	+ 1·0	Ag	3392·56	1	
3283·1	− 0·1	Ag	3283·00	10	ψ
3281·6	− 0·8	Ag	3280·80	10	ψ
3273·9	− 0·9	Au	3273·02	1	
3247·6	0·0	Cu	3247·60	10	ω
3122·9	0·0	Au	3122·88	10	χ
3034·4	− 0·2	Sn			
3029·5	− 0·2	Au	3029·30	6	
2995·6	− 0·5	Au	2995·13	6	
2990·4	0·0	Au	2990·38	4	

RING-MONEY : *Gold Sheath—continued.*

λ from curve.	Corr.	Element	λ	I.	P.
2954·9	− 0·3	Au	2954·64	6	
2907·2	0·0	Au	2907·18	5	
2825·0	+ 0·6	Au	2825·56	6	
2822·3	+ 0·6	Au	2822·87	5	
2820·7	− 0·6	Au	2820·11	10	
2802·5	− 0·2	Au	2802·35	10	
2795·4	+ 0·2	Au	2795·65	3	
2767·9	− 0·3	Ag	2767·64	50	χ
2755·3	+ 0·2	Ag	2755·50	20	φ
2749·2	− 0·3	Au	2748·90	1	
2747·9	+ 0·5	Au	2748·36	8	φ
2675·0	+ 1·1	Au	2676·08	8	χ
2644·6	+ 0·9	Au	2645·50	2	χ
2641·8	− 0·1	Au	2641·65	8	χ
2612·4	+ 0·4	Au	2612·80	1	χ
2607·5	− 0·1	Au	2607·40	1	
2600·0	− 0·5	Au	2599·50	2	
2584·8	− 1·3	Au	2583·50	2	
2506·9	− 0·2	Ag	2506·72	10	χ
2503·8	− 0·4	Au	2503·37	8	
2476·4	+ 0·4	Ag	2476·80	6	φ
2472·2	+ 1·1	Ag	2473·30	20	χ
2447·0	+ 0·4	Ag	2447·40	20	χ
2436·5	+ 0·8	Ag	2437·30	3	ψ
2426·6	+ 1·4	Au	2428·06	10	
2413·0	+ 0·3	Ag	2413·30	10	ω
	+ 0·3	Au	2413·27	3	
2411·3	0·0	Ag	2411·30	8	ψ
	+ 0·1	Au	2411·40	2	
2406·8	− 0·4	Ag	2406·40	1	
2396·1	− 0·4	Ag	2395·70	5	φ
	− 0·4	Au	2395·70	1	
2383·8	− 0·2	Ag	2383·60	2	φ
2380·5	0·0	Au	2380·50	1	
2369·8	+ 0·1	Cu	2369·90	10	χ
2357·3	+ 0·7	Ag	2358·00	8	χ
2334·0	+ 0·8	Sn			
2331·3	+ 0·2	Ag	2331·48	10	ψ
2325·1	+ 0·2	Ag	2325·30	6	ψ
2320·2	+ 0·3	Ag	2320·50	8	ψ
	+ 0·1	Au	2320·35	2	

RING-MONEY: *Gold Sheath—continued.*

λ from curve.	Corr.	Element	λ	I.	P.
2309·4	+ 0·1	Au	2309·54	6	
2304·6	+ 0·3	Au	2304·90	4	
2294·1	0·0	Au	2294·08	2	
2283·0	+ 0·4	Au	2283·37	6	
2280·7	− 0·6	Ag	2280·10	4	χ
2277·2	+ 0·4	Au	2277·62	4	
2269·0	0·0	Sn			
2248·7	+ 0·1	Ag	2248·81	6	χ
2247·1	0·0	Cu	2247·06	8	
2242·6	+ 0·2	Au	2242·80	3	
	+ 0·1	Cu	2242·69	6	χ
2229·4	+ 0·2	Ag	2229·65	3	φ
2215·6	+ 0·2	Au	2215·82	2	
2189·0	0·0	Au	2188·97	5	

II.—METALLIC ALLOY.

The subject of this examination was a metallic body found occasionally in small quantities in a certain brand of commercial calcium carbide. About 0·2 g. was available. Its specific gravity was between 9 and 10, and it conducted electricity like a metal. In appearance it resembled steel, but was quite brittle, and its hardness on Moh's scale was five. As regards the chemical nature and analysis of the substance, its great resistance to acid attack is of interest.

Spectrographic Analysis.

The alloy, when photographed, gave a spark spectrum containing many lines, but it was evident that the presence of iron accounted for most of them. A new photograph was taken of the unknown metal with a short slit, superposed on an iron spectrum with a long slit. In this way the long iron lines on the plate cancelled the lines of that element in the short spectrum.

There remained about forty lines. The distances of these lines from a known iron line were determined, referred to the interpolation curve, and the wave-lengths recorded. By means of tables of wave-lengths the lines were then completely identified.

The presence of iron, titanium, and silicon was proved.

In the following table details of the spectrographic analysis are recorded. The iron lines noted represent only very few of those occurring in the spectrum of the alloy, and have been measured solely as a check on the determinations of the lines of the other elements present. The corrections of wave-length found

for the iron lines have been applied to the measurement of other lines in their vicinity. In the last three columns are recorded the wave-lengths of the lines identified, together with their intensities (I), and persistencies (P), as determined for solutions of the elements concerned by Pollok and Leonard (Scient. Proc. R. Dub. Soc., 1907, **11**, p. 217), and Pollok (*ibid.*, 1909, p. 331):—

METALLIC ALLOY FOUND IN CALCIUM CARBIDE.

λ from curve.	Corr.	Element	λ	I.	P.
4548·0	+ 1·9	Ti	4549·90	20	ϕ
4101·5	− 0·5	Ti	4101·04	1	
4029·7	0·0	Fe			
3988·1	+ 1·8	Ti	3989·93	9	
3979·6	+ 2·3	Ti	3981·94	9	
3950·0	− 1·2	Ti	3948·84	8	χ
3932·1	+ 0·1	Ti	3932·22	4	
3905·4	− 0·4	Ti	3904·98	6	
3829·6	− 1·6	Fe			
3772·1	− 0·3	Ti	3771·80	3	
3687·1	− 1·7	Ti	3685·37	100	ω
3506·2	+ 1·1	Ti	3505·10	·30	χ
3460·0	+ 1·8	Ti	3461·71	10	χ
3438·8	+ 1·8	Fe			
3397·1	+ 1·6	Ti	3398·75	1	
3391·0	+ 1·1	Ti	3392·10	2	
3386·6	+ 1·4	Ti	3388·00	10	ϕ
3381·2	+ 1·6	Ti	3383·87	20	
3372·8	+ 0·1	Ti	3372·92	20	ω
3362·0	− 0·6	Ti	3361·40	30	
3351·0	− 1·5	Ti	3349·52	10	ω
3347·9	− 1·0	Ti	3346·92	5	ω
3341·9	− 1·4	Ti	3340·55	6	
3336·8	− 1·4	Ti	3335·39	10	ϕ
3331·0	− 1·2	Ti	3329·67	10	
3328·0	− 1·0	Ti	3326·99	5	ϕ
3280·1	− 1·0	Ti	3279·10	5	ϕ
3266·8	− 0·2	Ti	3266·55	1	
3261·3	− 0·9	Ti	3260·42	2	ψ
3255·4	− 1·0	Ti	3254·40	5	
3249·4	− 0·6	Ti	3248·79	10	ϕ
3244·0	− 1·8	Ti	3242·19	10	χ
3240·4	− 0·5	Ti	3239·86	4	χ
3215·1	− 0·2	Ti	3214·89	3	

METALLIC ALLOY FOUND IN CALCIUM CARBIDE—*continued.*

λ from curve.	Corr.	Element	λ	I.	P.
3202·0	+ 0·7	Ti	3202·68	10	χ
3106·9	− 1·6	Ti	3105·22	3	
3087·6	+ 0·6	Ti	3088·17	10	χ
3080·0	− 1·3	Ti	3078·70	6	χ
2925·3	+ 1·3	Fe			
2883·2	+ 1·1	Ti	2884·29	8	ϕ
2664·2	+ 2·4	Fe			
2662·2	+ 2·5	Fe			
2526·1	+ 2·5	Si	2528·60	8	ψ
2514·2	+ 2·1	Si	2516·26	10	ψ
2504·4	+ 2·6	Si	2507·01	6	ϕ

Chemical Analysis.

Mineral acids and fused potassium pyrosulphate were without appreciable action on the substance; but on prolonged fusion with sodium peroxide it was attacked. For the silicon estimation the Drown Method was adopted. This depends on the volatilization of the element as silicon tetrafluoride, titanium tetrafluoride not being volatilized under the same conditions. For the separation of the iron and titanium, advantage is taken of the relatively high solubility in ether of ferric chloride compared with the titanic compounds.

The results are set out below:—

Weight of alloy	... 0·1936 g.			
„ „ silicon dioxide	... 0·0499 g.	giving silicon	...	11·3 %
„ „ titanic oxide	... 0·0711 g.	„ titanium	...	22·0 %
„ „ ferric oxide	... 0·1830 g.	„ iron	...	66·2 %

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No. 8.

"BLOSSOM-WILT" OF APPLE TREES AND "WITHER-TIP" OF PLUM TREES, WITH SPECIAL REFERENCE TO TWO BIOLOGIC FORMS OF *MONILIA CINEREA* BON.

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(Plates 3, 4, and 5.)

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Introduction.

It has long been known to horticulturists and plant pathologists that the fruits of the cultivated species of *Pyrus* and *Prunus* are frequently attacked by fungi, which, gaining access to the cells of the fruit through wounds, rapidly develop within the tissues, and produce a discoloration of affected cells. Owing to the nature of the injury effected, the causal organisms were generally referred to as the "brown-rot" fungi.

The first published account of "brown-rot" of fruits appeared in 1796, when Persoon (7) gave the name *Torula fructigena* to a fungus which he found on decayed fruits of *Prunus domestica* (European plum), *Amygdalis perisca* (peach), and *Pyrus communis* (French pear). In 1801 Persoon changed the name to *Monilia fructigena*, which name is still in use.

Bonorden (4), in 1857, introduced the name *Monilia cinerea* for a fungus which he found on decayed fruits.

Schröter (9), in 1893, concluded that both *Monilia fructigena* and *Monilia cinerea* were conidial stages of an ascomycete, and transferred them to the genus *Sclerotinia*.

Woronin (14), in his well-known papers of 1898–9, submitted convincing proof that *Sclerotinia fructigena* and *S. cinerea* could be readily distinguished, even in the Monilia stage. Other investigators, however, refused to accept his conclusions, and considered that "brown-rot" diseases of cultivated fruit-trees were caused by one species only, viz., *Monilia fructigena*.

Aderhold, in 1904, discovered the apothecial stage of *Monilia fructigena*, thus confirming Schröter's conclusion regarding the ascomycetous nature of the

fungus. Norton (6) had, two years previously, found apothecia which had developed from mummified peaches; this form Norton himself referred to *Sclerotinia fructigena,* but Aderhold and Ruhland (2) in 1905 concluded that it was *Sclerotinia cinerea.*

Salmon (8), in 1907, recorded outbreaks of "brown-rot" on acid cherries, and in 1910–14 called attention to a serious "brown-rot" disease which destroyed the blossom of apple trees, invaded the branches, and sometimes produced cankers.

Eriksson (5), in 1913, figured and described a canker-like disease of apple trees. He concluded that there was no distinction between *M. fructigena* and *M. cinerea,* and assumed that the form appearing on the fruit in autumn was a stage in the annual cycle of that form which kills the twigs and blossoms.

Wormald (10), in 1917, undertook the investigation of epidemic attacks of the "Blossom-Wilt and Canker" disease of apple trees, and made by far the most important contributions to our knowledge of these diseases. He found that the fungus responsible was not *Monilia fructigena,* which had been assumed to be the species causing the disease, but *Monilia cinerea,* Bon. Later, in 1918, a "Wither-Tip" of plum trees was found to be caused by a fungus morphologically similar to that causing "Blossom-Wilt and Canker" disease of apple trees, but differing from it biologically in that it was unable to establish itself in the flowering spurs of the apple. He was, therefore, led to differentiate between two distinct forms of *M. cinerea,* which he distinguished as *M. cinerea, forma mali,* causing "Blossom-Wilt and Canker" disease of apple trees; and *M. cinerea, forma pruni,* causing a "Wither-Tip" of plum trees.

The present investigation arose out of a report of the presence of a disease on plum trees in the summer of 1922 in the orchard of the Munster Institute, Cork. The variety "Czar" was severely affected, the variety "Victoria" slightly affected. The disease was noticed on the fruit when the latter was about three-quarters ripe. The fruit remained sour at maturity. The following spring (1923), young shoots of apple trees, of the varieties "Cox's Orange Pippin" and "Worcester Pearmain," growing near the plum trees, were noticed to wither back when they had made 3″ or 4″ growth. At that time there was no apparent evidence of the disease on the spurs. Later in the year, these young shoots developed pustules of *Monilia cinerea.*

The above observations suggested that the disease, which first occurred on plum trees, was transferred to apple trees, and was able, contrary to Wormald's observations, to produce a "Blossom-Wilt" of the latter.

The object of the present investigation was to ascertain whether there were two distinct forms of *Monilia cinerea* in Ireland, causing "Blossom-Wilt" of apple trees and "Wither-Tip" of plum trees, respectively, as described by Wormald as occurring in England.

For this purpose pure cultures were prepared from naturally infected apple and plum trees, and the cultural characteristics on various artificial media compared. Inoculation experiments were also carried out on both apple and plum trees.

Cultural Studies.

Cultures were obtained (*a*) from single spores, (*b*) from the mycelium of the fungus in the wood of infected trees. When the fungus occurred as barren mycelium only, transverse sections were made through the infected part with a sterilized razor.

(*a*) A sterile platinum wire was gently rubbed to one of the pustules. This was dipped into a test tube containing about 5 c.c. of sterile water, and a suspension of spores was thus obtained. One drop of this suspension was examined under the microscope, and, if too concentrated, a single drop of the suspension was added to a second test tube of sterile water. When the dilution was such that one drop contained a single spore, a single drop was transferred to a Water-Agar plate (3% Agar) by means of a sterilized platinum loop. When the spore germinated, and was found to be uncontaminated, it was transferred to a plate of Nutrient Agar. This transference was made in a sterile chamber, which had been sprayed with a solution of Mercuric Chloride of concentration 1 in 1,000. When the mycelium grew out, portions from the periphery were transferred to other artificial media.

(*b*) Sections of diseased wood when examined under the microscope showed the fungus ramifying through the tissues (Pl. 3, fig. 6), as when pure cultures were required from such sources, transverse sections of infected wood were made with a sterilized razor. These sections were placed in sterile water, and particles of a section were teased out, and placed on Agar plates. The mycelium present in the tissues usually grew out uncontaminated, but, to ensure purity of culture, sub-cultures from the peripheral portion of the mycelium were transferred to other prepared media.

Mode of Growth on Culture Media.

The following table shows a marked difference between the "Blossom-Wilt" Monilia and the "Wither-Tip" Monilia in their characteristic mode of growth on culture media. These cultures were kept at a temperature of 32° C. At this temperature they did not produce spores. All sugar-containing media (hexoses or polyoses) gave extremely good growths.

TABLE 1.

Medium.	Growth characteristics of "Wither-Tip" fungus isolated from plum. Variety, "Victoria."	Growth characteristics of "Blossom-Wilt" fungus isolated from apple. Variety, "Cox's Orange Pippin."
Steamed Potato.	Greyish colour. Downy growth.	Greyish-white colour. Downy growth.
Czapek Agar.	Greyish colour. Very good growth. No concentric rings. Lobed at periphery.	Greyish colour. Very good growth. Concentric rings formed. Not lobed at periphery.
Saccharose Synthetic Agar.	Greyish colour. Downy growth. No concentric rings formed. Lobed at periphery.	White colour. Concentric rings formed. Not lobed at periphery.
Glucose Broth.	Greyish colour. Good growth. Concentric rings very narrow. Lobed at periphery.	White colour. Exceedingly good growth. Concentric rings formed. Not lobed at periphery.
Krainsky's Dextrose Agar.	Greyish colour. Good growth. Concentric rings formed. Lobed at periphery.	White colour. Very good growth. Rings poorly developed. Not lobed at periphery
Dextrose Synthetic Agar.	Greyish colour. Good downy growth. No concentric rings formed. Lobed at periphery.	White colour. Very good growth. Concentric rings formed. Not lobed at periphery.
Coon's Synthetic Agar.	Greyish-white colour. Very flat mycelium. Slight formation of concentric rings. Lobed at periphery.	White colour. Very flat growth. Concentric rings formed. Not lobed at periphery.
Glycerine Synthetic Agar.	Greyish colour. Growth very poor. Concentric rings formed.	Whitish colour. Very flat growth. Rings feebly developed.
Nutrient Potato Agar.	Grey colour. Very flat mycelium. Concentric rings formed. Lobed at periphery.	White colour. Growth meagre. Concentric rings well developed. Not lobed at periphery.
Bacto-beef medium.	Greyish colour. Very flat growth. Lines radiating from point of inoculation to periphery. No concentric rings.	Greyish-white colour. Growth poor. Concentric rings formed.
[1]Brown's Synthetic medium (A).	Greyish colour. Good downy growth. No concentric rings formed. Lobed at periphery.	White colour. Very poor growth. No ring-like development. Not lobed at periphery.
[1]Brown's Synthetic medium (B).	Greyish colour. Growth poor. Lobed at periphery.	Whitish colour. Growth poor. Not lobed at periphery.

[1] Annals of Botany, 1925, 39, pp. 373–408.

As shown in Table 1, the most characteristic difference between the "Wither-Tip" and "Blossom-Wilt" forms of Monilia on the various media was the tendency of the former to grow out into lobes at the periphery, while the latter produced a uniform circular growth. The "Blossom-Wilt" form was usually lighter in the colour than the "Wither-Tip" variety, and showed a greater tendency to form concentric rings.

Dimensions of Pustules.

The dimensions of pustules taken from diseased apple and plum twigs and mummied fruits were found to be variable.

TABLE 2.

Source of Pustules.	Average dimensions in millimetres.	Range of variation in millimetres.
Mummied Plum.		
Variety, "Victoria." . . .	2·0 × 1·25	1·0 × 1·0 to 3·0 × 1·0
Twig of Plum tree.		
Variety, "Victoria." . . .	1·5 × 1·0	1·0 × 0·75 to 2·5 × 1·5
Twig of Apple tree.		
Variety, "Cox's Orange Pippin."	1·5 × 1·5	1·0 × 1·0 to 2·5 × 2·0
„ "Lane's Prince Albert."	2·0 × 1·5	1·5 × 1·5 to 3·0 × 1·5
„ "Loddington." . .	2·0 × 1·0	1·5 × 1·0 to 2·0 × 1·5

Dimensions of Conidia.

When conidia were obtained from pustules, they were always taken from the outer layers, in order to ensure that they had attained full development.

TABLE 3.

Source of Conidia.	Variety.	Average of 100 conidia in microns.	Range of variation in microns.
"Blossom-Wilt" Monilia obtained from Apple Trees.			
Canker.	"Lane's Prince Albert."	11·7 × 8·0	7·5 × 6·0 to 15·1 × 10·6
Dead Spur.	"Cox's Orange Pippin."	11·3 × 8·5	7·5 × 6·0 to 13·6 × 10·6
Steamed Potato.	"Lane's Prince Albert."	15·5 × 12·4	8·7 × 8·0 to 27·4 × 17·5
Steamed Potato.	"Cox's Orange Pippin."	15·7 × 12·7	8·0 × 8·0 to 25·0 × 18·0
"Wither-Tip" Monilia obtained from Plum Trees.			
Dead Spur.	"Victoria."	12·3 × 8·7	10·0 × 6·0 to 20·0 × 12·0
Steamed Potato.	"Victoria."	13·3 × 10·2	8·0 × 8·0 to 25·0 × 25·0

The conidia obtained from pure cultures were larger than those found on pustules taken from diseased trees. There was very little difference in size, however, between "Wither-Tip" and "Blossom-Wilt" conidia, whether obtained from pustules produced on diseased wood or from artificial media.

Effect of Temperature on Sporulation.

Sporulation of the fungus presented great difficulties at the beginning of the investigation.

Cultures kept at a temperature of 32° C. did not sporulate, which fact suggested that the temperature may have some effect on spore production. Those kept at room temperature, which was about 9° C., produced spores readily. This result led to further work on the effects of temperature on spore production, the results of which are seen below.

The cultures were grown on Steamed Potato, Czapek Agar, Glucose Broth, and Coon's Medium.

TABLE 4.

Medium.	Source from which pure culture was obtained.	8° C.–9° C.	14° C.–15° C.	20° C.	26° C.	32° C.
Steamed Potato.	*Plum.* (Variety, "Victoria.")	Sporulating very well.	Sporulating very well.	Sporulating well.	Sporulating fairly well.	Not Sporulating.
	Apple. (Variety, "Cox's Orange Pippin.")	Sporulating very well.	Sporulating very well.	Sporulating fairly well.	Sporulating poorly.	Not Sporulating.
Czapek Agar.	*Plum.* (Variety, "Victoria."	Sporulating well.	Sporulating fairly well.	Sporulating very poorly.	Sporulating poorly.	Not Sporulating.
	Apple. (Variety, "Cox's Orange Pippin.")	Sporulating well.	Not Sporulating.	Not Sporulating.	Sporulating poorly.	Not Sporulating.
Glucose Broth.	*Plum.* (Variety, "Victoria.")	Sporulating very well.	Sporulating fairly well.	Sporulating very poorly.	Not Sporulating.	Not Sporulating.
	Apple. (Variety, "Cox's Orange Pippin.")	Sporulating very poorly.	Not Sporulating.	Not Sporulating.	Not Sporulating.	Not Sporulating.
Coon's Synthetic Medium.	*Plum.* (Variety, "Victoria.")	Sporulating very well.	Sporulating very well.	Sporulating fairly well.	Not Sporulating.	Not Sporulating.
	Apple. (Variety, "Cox's Orange Pippin.")	Sporulating well.	Not Sporulating.	Not Sporulating.	Not Sporulating.	Not Sporulating.

The above results show that temperature affects sporulation to a very marked degree. Sporulation increases as the temperature decreases. The lowest temperature available (6° C.–9° C.) was most favourable to spore production.

Sporulation of the forms of the fungus isolated from apple and plum were, on the whole, similarly affected by temperature.

Inoculation Experiments.

For inoculation experiments young apple and plum trees were obtained. Some of these were placed in the greenhouse, with the result that the flowers opened about the middle of March. The remainder, which were left in the open, were not ready for inoculation until a month later.

Conidia for inoculation purposes were obtained from cultures on steamed potato. The potato wedge with its conidia was removed to a sterile Petri dish. Small portions were cut off with flamed scalpels, and transferred to another sterile dish. The actual inoculation of the flower was made by removing from the dish one of the particles of potato on the point of a sterilized platinum needle, and the conidia-bearing surface applied to the stigma of the flower. This method was adopted to prevent injury to the stigmatic surface.

Experiments on those flowers which had just opened were found to give better results than those which had been expanded for some time.

The untreated trusses served as controls.

The following inoculation experiments were carried out:—

(1) Flowers of apple tree inoculated with a pure culture of "Blossom-Wilt" Monilia.

(2) Flowers of apple tree inoculated with a pure culture of "Wither-Tip" Monilia.

(3) Flowers of plum tree inoculated with a pure culture of "Wither-Tip" Monilia.

(4) Flowers of plum tree inoculated with a pure culture of "Blossom-Wilt" Monilia.

Results of Inoculation Experiments.

In all, ninety inoculation experiments were carried out, of which fifty-four were successful. To avoid repetition, one example of each is given in detail. No essential difference was perceptible between outdoor and indoor experiments in susceptibility to disease, progress, and results.

(1) Flower of Apple inoculated with "Blossom-Wilt" Monilia. Variety, "Ecklinville Seedling."

Inoculated with pure culture isolated from Apple (Variety, "Cox's Orange Pippin").

One flower on truss of five inoculated April 15th.

After 6 days—Styles brown for a length of 5 m.m.
„ 11 „ —Styles brown to base. Stamens drooping.
„ 13 „ —Pedicel brown almost to base.
„ 17 „ —Remaining pedicels on truss brown from base upwards for a length of ½ inch.
„ 19 „ —Truss drooping. Petioles of leaves brown from base upwards for length of ¼ inch.
„ 22 „ —Leaves brown. Truss wilting.
„ 7 weeks—Canker extending down branch for a length of 5 inches.
„ 9 months—Pustules on spur.

(2) Flower of Apple inoculated with "Wither-Tip" Monilia. Variety, "Bramley's Seedling."

Inoculated with pure culture isolated from Plum (Variety, "Victoria"). One flower on truss of six inoculated April 12th.

After 7 days—Styles brown for a length of 2 m.m.
„ 9 „ —Styles brown almost to base.
„ 13 „ —Styles brown to base.
„ 25 „ —Flower detached at base of pedicel.

Further observations showed no development of the disease.

(3) Flower of Plum inoculated with "Wither-Tip" Monilia. Variety, "Dennison's Superb."

Inoculated with pure culture isolated from Plum (Variety, "Victoria"). One flower on truss of two inoculated April 7th.

After 4 days—Style brown for a length of 3 m.m.
„ 7 „ —Style brown to base.
„ 12 „ —Pedicel brown to base.
„ 14 „ —Pedicel of remaining flower brown from base upwards for a length of ¼ inch. Pustules on style.
„ 20 „ —Leaves around the base of the inflorescence showed a characteristic withering at the tips.
„ 10 months—Pustules on spur.

(4) Flower of Plum inoculated with "Blossom-Wilt" Monilia. Variety, "Victoria."

Inoculated with pure culture isolated from Apple (Variety, "Lane's Prince Albert").

Flower inoculated April 4th.

After 8 days—Style brown for a length of 4 m.m.
„ 11 „ —Style brown to base.
„ 15 „ —Petals wrinkled, and turning brown.
„ 19 „ —Flower dead. Pedicel unaffected.

Later observations showed pedicel quite healthy.

The results obtained in the remaining successful inoculation experiments were in conformity with those described above, and showed in an unmistakable manner the difference in the behaviour of "Blossom-Wilt" and "Wither-Tip" Monilia. When flowers of apple trees were inoculated with "Blossom-Wilt" Monilia, the fungus invaded the style, and by the end of two weeks had travelled to the base of the pedicel, turning it brown.

The remaining pedicels on the truss turned brown from the base upwards, and by the end of three weeks all the flowers on the truss were killed.

Cankers developed later, and in the course of two or three months had enveloped several inches of the infected branches. Apple trees inoculated with "Wither-Tip" Monilia, however, were in very marked contrast to above. In the initial stages, the progress of infection was similar to that described, viz., the styles of infected flowers turned brown to the base, but the similarity in behaviour ended here. By the end of three to four weeks, the pedicels bearing infected flowers became detached, and the disease made no further progress. The "Wither-Tip" fungus was unable to establish itself on apple trees.

Infection experiments on plum trees gave parallel results. Flowers of plum trees inoculated with the "Wither-Tip" fungus were soon killed. The fungus travelled down the pedicel, the petioles of the leaves turned brown, and infected branches presented a typical "Wither-Tip" appearance. Flowers of plum trees inoculated with "Blossom-Wilt" fungus behaved very differently. The actual flowers infected were killed; the pedicels bearing these remained quite green. The remaining flowers on the truss developed normally. In all cases the controls remained healthy.

Convincing evidence was, therefore, obtained that there are two forms of *Monilia cinerea,* which are morphologically similar, but physiologically different, as shown by their behaviour on culture media, and also in infection experiments, thus confirming the results obtained by Wormald.

Control Experiments.

The control experiments were carried out on trees in the orchard attached to the College farm, also on trees grown in the College grounds.

The orchard contains about twenty apple trees, arranged in four rows. Five of these trees were severely attacked with *Monilia cinerea, forma mali,* causing typical "Blossom-Wilt," while three others were moderately affected. The remaining trees showed little or no sign of the disease.

Four different methods of control were adopted, viz.:—

(1) Spraying with a solution of Caustic Soda and Soft Soap.
(2) Spraying with Potassium Carbonate, Caustic Soda, and Soft Soap.
(3) Spraying with Carbo-crimp.
(4) Removal of dead spurs bearing pustules.

(1) Two trees, which were very badly infected, were sprayed with a solution of 1 % Caustic Soda and 1 % Soft Soap a short time before the flowers opened, but in time to prevent injury to the young shoots (February, 1928). Examination of the trees the first week in June showed that such treatment was very ineffective as a control measure, the trees having fifty-five and twenty-four diseased trusses, respectively.

(2) Six apple trees artificially inoculated with *Monilia cinerea, forma mali,* in April, 1927, were also utilised for spraying experiments in 1928. These were sprayed with a solution of $\frac{3}{4}$ lb. Commercial Potassium Carbonate, 1 lb.

Caustic Soda, and 10 ozs. Soft Soap in 10 gallons of water. There was no apparent improvement as a result of the treatment. The number of diseased trusses found in 1928 corresponded approximately with the number artificially inoculated in 1927.

(3) Four trees were sprayed with a solution of Carbo-crimp. Here again the treatment was ineffective, the trees having thirty-six, fifty-four, ten, and eighteen diseased trusses, respectively, when examined the first week in June.

(4) In February, 1928, all infected spurs from one side of each of two trees, which were uniformly infected, were removed. Observations made four weeks after the flowers had opened showed a marked improvement. On one tree only four diseased trusses were found on the side from which the dead spurs were removed, while there were nineteen on the other side. On the other tree a similar condition obtained, there being no infected trusses on the side from which the dead spurs had been removed, while five were found on the other side, which acted as a control.

Six trees artificially inoculated with *Monilia cinerea, forma mali,* in April, 1927, were also used for control experiments in 1928. All diseased spurs were removed in February, and the disease effectively checked, as there was not a single diseased truss to be found the following June.

Spraying with the solutions utilised in these experiments was useless as a method of control of apple blossom-wilt, even when spraying was delayed as late as possible before the flowers opened. Removal of diseased spurs, on the other hand, proved a very effective method of control. This operation should be carried out some time before the flowers expand, and the trees should be examined again after they have come into flower. Any wilted trusses present should be removed, as these serve as centres of infection the following season. Diseased trusses should be burned immediately on removal.

The authors desire to express their thanks to the Royal Dublin Society for a grant for the purchase of materials and apparatus utilised in these investigations, also to the Department of Lands and Agriculture, for facilities offered for experimental work in the orchard at the Munster Institute, Cork.

Summary.

1. Conidia taken from *M. cinerea* causing "Wither-Tip" of plums are larger than those of *M. cinerea* causing "Blossom-Wilt" of apples when taken from a dead spur. When grown on culture media, the results are reversed.

2. At a temperature of 32° C. neither form sporulates, but at temperatures ranging from 8° C. to 26° C. "Wither-Tip" Monilia sporulates better than "Blossom-Wilt" Monilia. In both cases, sporulation decreases with rise of temperature, the maximum amount of spores having been produced at the lowest temperature available, viz., 6° C.–9° C.

3. The two forms differ considerably in cultural characteristics. "Wither-Tip" Monilia is grey in colour, and is generally lobed at the periphery; while

"Blossom-Wilt" Monilia is white, and has a peculiar formation of concentric rings.

4. When apple flowers are inoculated with a pure culture of "Blossom-Wilt" Monilia, the fungus travels through the style and pedicel. When it reaches the base of the pedicel, it travels upwards through the pedicels of the remaining flowers of the inflorescence, and through the petioles of the leaves, ultimately producing a wilting of the entire truss.

5. When apple flowers are inoculated with a pure culture of "Wither-Tip" Monilia, the actual flower inoculated becomes detached at the base of the pedicel. No other flower of the inflorescence is affected.

6. When plum flowers are inoculated with a pure culture of "Wither-Tip" Monilia, the fungus travels through the style and pedicel of the flower. When it reaches the base of the pedicel it travels upwards through the pedicels of the remaining flowers of the inflorescence through the petioles of the leaves, ultimately producing a typical wither-tip of the leaves.

7. When plum flowers are inoculated with a pure culture of "Blossom-Wilt" Monilia, only the actual flower inoculated is killed. The fungus only penetrates as far as the base of the style. No other flower of the inflorescence is affected.

8. The results of culture and infection experiments, using the "Wither-Tip" and "Blossom-Wilt" forms of *Monilia cinerea,* show that the two forms are physiologically different. These results are in conformity with those of Wormald, and justify the distinction *forma mali* and *forma pruni* for the forms occurring on apple and plum, respectively.

9. Various spray mixtures were used for control purposes, but all proved very ineffective. The best results were obtained by removing and subsequently burning diseased spurs and trusses.

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DESCRIPTION OF PLATES.

Plate 3.—Drawings.

Fig.

1. Spore germinating on Pure Juice Gelatine after 18 hours. (× 800.)
2. Spore germinating on Czapek Agar after 18 hours. (× 800.)
3. Spore germinating on Prune Juice Gelatine after 24 hours. (× 800.)
4. Spore germinating on Czapek Agar after 24 hours. (× 800.)
5. Chain of spores produced on Prune Juice Gelatine. (× 800.)
6. Hypha seen running through an annular vessel of xylem in longitudinal section of diseased twig of apple tree. (× 800.)
7. Chain of spores produced on Prune Juice Gelatine. (× 300.)
8. Chain of spores produced on Steamed Potato. (× 430.)

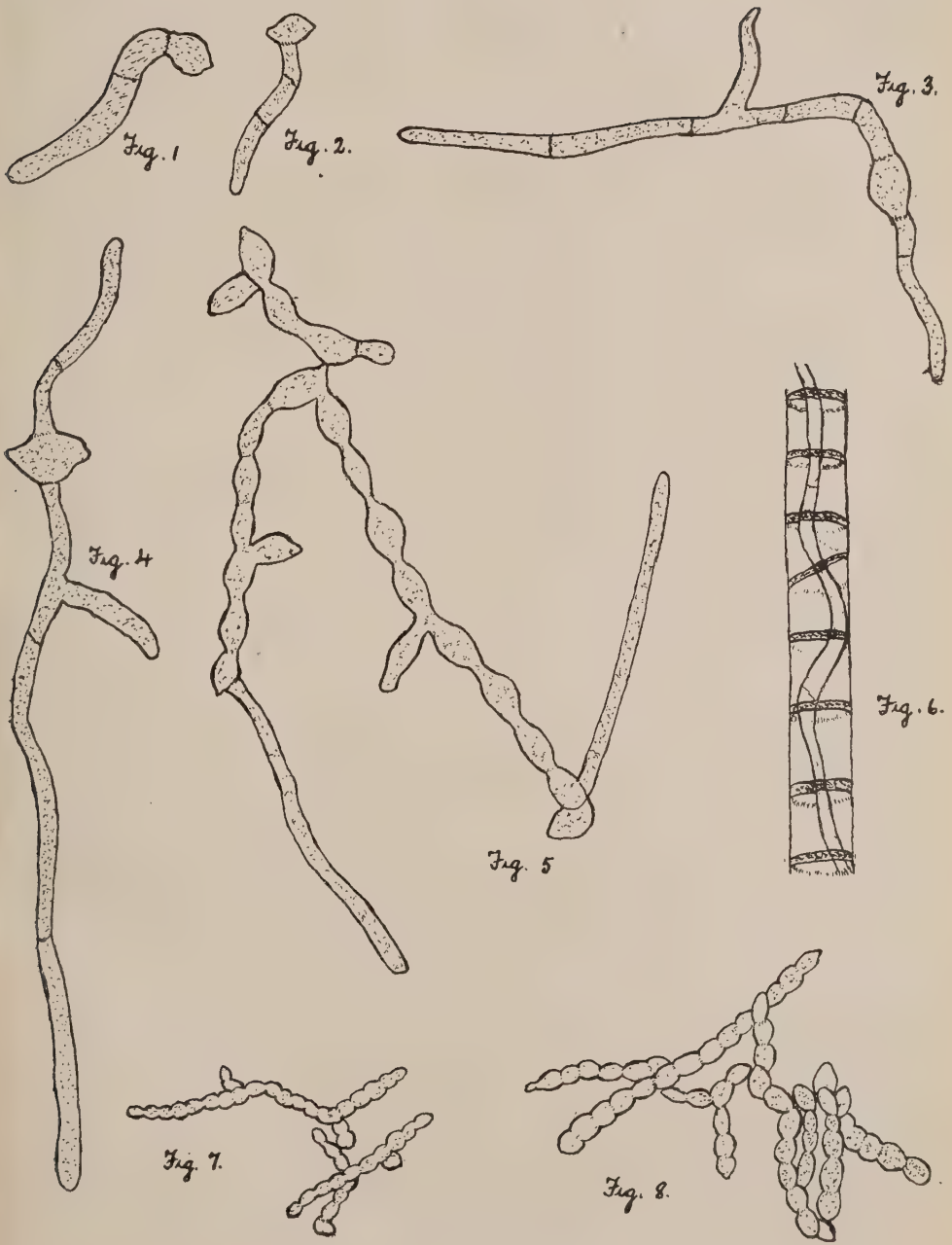
Plate 4.—Photographs.

1. Diseased apple twig showing pustules.
2. Mummied plum with pustules.
3. Culture of *Monilia cinerea, forma mali,* on Glucose Broth.
4. Culture of *Monilia cinerea, forma pruni,* on Glucose Broth.
5. Result of inoculation of apple flower with pure culture of *Monilia cinerea, forma mali,* showing typical "Blossom-Wilt" condition.
6. Result of inoculation of plum flower with pure culture of *Monilia cinerea, forma mali,* showing only withering of flower actually inoculated. The disease does not penetrate the pedicel.

PLATE 5.—PHOTOGRAPHS.

Fig.

1. Result of inoculation of plum flower with pure culture of *Monilia cinerea, forma pruni,* showing typical "Wither-Tip" condition.
2. Result of inoculation of apple flower with pure culture of *Monilia cinerea, forma pruni,* showing the inoculated flower detached from base of pedicel.
3. Canker formed on twig of apple tree about a month after inoculation.
4. Foliage distal to canker wilting.
5. Close-up view of canker on apple tree.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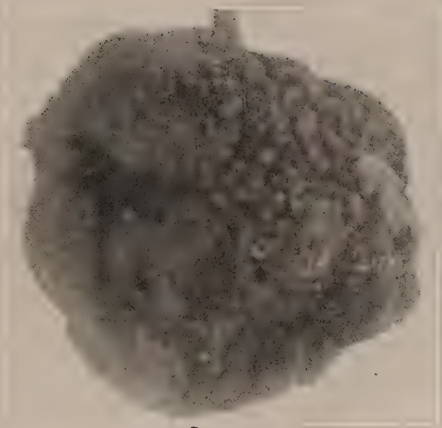

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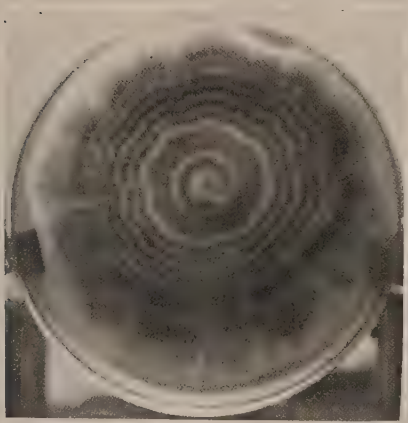

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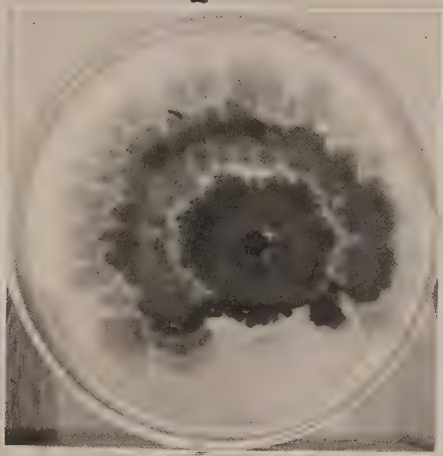

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No. 9.

A SYNTHESIS OF 5 : 7 : 2′ : 4′–TETRAHYDROXYFLAVONE AND OF 7 : 2′ : 4′ : 6′–TETRAHYDROXYFLAVONE.

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AND

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[Read May 22. Published separately November 1, 1928.]

Lotoflavin is a yellow colouring matter found in an Egyptian plant, *Lotus arabicus*, from which it was isolated by Dunstan and Henry (Phil. Trans. Roy. Soc., 1901, **194**, p. 515). It is present in the plant as a glucoside, lotusin, which on hydrolysis is converted into lotoflavin, dextrose, and hydrocyanic acid.

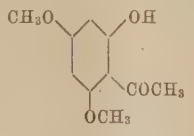
$$C_{28}H_{31}O_{16}N + 2H_2O = C_{15}H_{10}O_6 + 2C_6H_{12}O_6 + HCN.$$

The colouring matter was found to resemble the flavones in properties, and on fusion with potassium hydroxide it gave phloroglucinol and β-resorcylic acid, whence it was assigned the formula (IV), 5 : 7 : 2′ : 4′-tetrahydroxyflavone. This substance has not previously been obtained synthetically, but its synthesis has now been carried out as follows:—

Phloroglucinol trimethyl ether, on treatment with acetyl chloride and ferric chloride, gave phloroacetophenone trimethyl ether. This compound, by the action of aluminium chloride, was converted into phloroacetophenone 4 : 6-dimethyl ether (I). Methyl 2 : 4-dimethoxybenzoate (II) was next prepared by the methylation of β-resorcylic acid with dimethyl sulphate. By the condensation of the ester (II) with the dimethyl ether (I) in the presence of sodium 2-hydroxy-4 : 6 : 2′ : 4′-tetramethoxybenzoylacetophenone (III) was produced. The last-named compound, on treatment with hydriodic acid for a short time, yielded 5 : 7 : 2′ : 4′-tetramethoxyflavone, which on demethylation by means of the same reagent gave 5 : 7 : 2′ : 4′-tetrahydroxyflavone (IV). This substance was also obtained by the action of hydriodic acid on the ketone (III).

The synthetic flavone (IV) and the naturally occurring compound, lotoflavin (a specimen of which has been kindly given us by Dr. Harold Brown), were both found to consist of small bright-yellow plates, very similar in appearance. Other properties of the two substances were also investigated, and found to be alike (see Experimental Part). Neither substance melted sharply; the synthetic compound commenced to darken at about 270°, becoming black at about 300°.

The natural compound also began to turn dark at about 270°, decomposing at about 315°. A more suitable comparison would have been the corresponding tetramethoxyflavones. 5 : 7 : 2′ : 4′-Tetramethoxyflavone, obtained synthetically as described above, possesses a sharp melting-point, but methylation of the natural colouring matter by Dunstan and Henry (*loc. cit.*) furnished not the tetramethoxy derivative, but a mixture of α- and β-trimethyl ethers.



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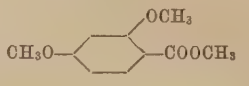

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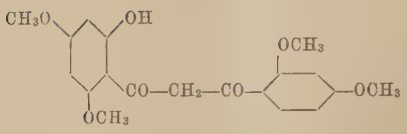

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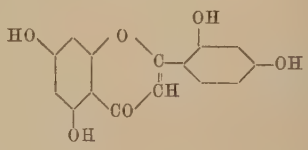
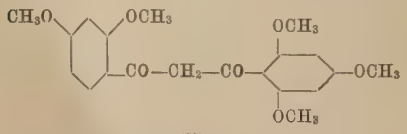


(IV)

A synthesis of 7 : 2′ : 4′ : 6′-tetrahydroxyflavone (VI) was also carried out by a similar series of reactions. Phloroacetophenone trimethyl ether on condensation with methyl 2 : 4-dimethoxybenzoate in presence of sodium gave 2 : 4 : 6 : 2′ : 4′-pentamethoxybenzoylacetophenone (V), and this compound, when treated with hydriodic acid, was converted into 7 : 2′ : 4′ : 6′-tetramethoxyflavone. It was theoretically possible in this reaction for the formation of the pyrone ring to take place in two ways, with the production of 5 : 7 : 2′ : 4′-tetramethoxyflavone (corresponding to IV), and 7 : 2′ : 4′ : 6′-tetramethoxyflavone (corresponding to VI), but actually only one of these two bodies was obtained, and as it was a completely distinct substance from 5 : 7 : 2′ : 4′-tetramethoxyflavone, it could only be 7 : 2′ : 4′ : 6′-tetramethoxyflavone. The last-mentioned compound or the pentamethoxybenzoylacetophenone (V) on treatment with hydriodic acid yielded 7 : 2′ : 4′ : 6′-tetrahydroxyflavone (VI).



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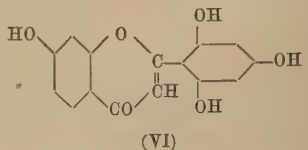

(VI)

Other syntheses of these flavones by one of us (N.M.C.) are also in progress.

Experimental.

Phloroacetophenone 4 : 6-Dimethyl Ether (I).

This compound is briefly described by Friedländer and Schnell (Ber. d. Deutsch. Chem. Ges., 1898, **30**, p. 2152; compare Kostanecki and Tambor, *ibid.*, 1900, **32**, p. 2262). The method adopted in the present work was as follows:—

The trimethyl ether of phloroacetophenone (Kostanecki and Tambor, *loc. cit.*; compare Freudenberg, Ber. d. Deutsch. Chem. Ges., 1921, **53**, p. 1425) was mixed with an equal weight of freshly sublimed aluminium chloride, and the mixture was heated in an oil bath at 110° for 30 minutes. The flask was then cooled, water was added, and the supernatant liquid after acidification was decanted from the dark oily product. The latter was extracted with boiling ligroin, on evaporation of which an almost pure compound resulted. This was recrystallized from dilute alcohol, from which it separated out in colourless plates, melting at 82°. The yield was about 50 %. The product was insoluble in water, soluble in the usual organic solvents, and in alkali.

Methyl 2 : 4-Dimethoxybenzoate (II).

This substance has been obtained by the methylation of β-resorcylic acid in the cold with dimethyl sulphate and dilute aqueous sodium hydroxide (Perkin and Schliess, Jour. Chem. Soc., 1904, **85**, p. 159). We found the following modification more satisfactory (80 % yield):—

β-Resorcylic acid (10 g.) was mixed with dimethyl sulphate (57 c.c.) and potassium hydroxide (34 g. in an equal weight of water) was added in small portions. After each addition the flask was vigorously shaken (and cooled if necessary) until a test portion of the mixture ceased to give an alkaline reaction. The temperature was maintained at about 50° throughout the experiment. When all the potassium hydroxide had been added, the mixture on further shaking remaining alkaline, the product was extracted immediately with ether, the ethereal solution was washed with dilute aqueous sodium hydroxide, then with water, and left to dry over calcium chloride. The ester was obtained pure by distillation under diminished pressure. It is a colourless liquid, boiling under atmospheric pressure at 295°.

2-Hydroxy-4 : 6 : 2′ : 4′-tetramethoxybenzoylacetophenone (III).

Three grams of phloroacetophenone 4 : 6-dimethyl ether and 1·4 molecular proportions of methyl 2 : 4-dimethoxybenzoate were added to a flask containing anhydrous ether and 2 molecular proportions of finely divided sodium. (The sodium was first melted under hot xylene and then vigorously shaken, when the metal was obtained in a very fine condition.) The ether was then evaporated off, and the oily mixture was heated on a boiling-water bath in a flask fitted with a stopper containing a tube filled with calcium chloride. Vigorous reaction, lasting for a short time, ensued, and when it had subsided, the flask

contents were heated to 150°–160°, and maintained at that temperature for 2 hours, being shaken from time to time. The product was allowed to cool, and was then shaken up with very dilute aqueous sodium hydroxide, the solution being separated by decantation through a filter from the oily solid. On acidification of the filtrate with 5 % acetic acid, a turbid precipitate was deposited. The product was allowed to remain at the room temperature for 24 hours, when the liquid was removed by filtration. The solid was washed with water, and crystallized from boiling alcohol. Colourless plates, melting at 151°, were obtained in moderate amount. The following results were obtained on analysis :—

0·1223 g. of the substance gave 0·2817 g. of CO_2 and 0·0650 g. of H_2O,
corresponding to C 62·8, H 5·9.
$C_{19}H_{20}O_7$ requires C 63·3, H 5·6 %.

2-Hydroxy-4 : 6 : 2′ : 4′-tetramethoxybenzoylacetophenone in alcohol solution gives an olive-green coloration with a drop of ferric chloride. The solution in sodium hydroxide is colourless. On addition of concentrated sulphuric acid the crystals first become orange-red and then dissolve, giving a yellow solution.

5 : 7 : 2′ : 4′-Tetramethoxyflavone.

To 4 g. of the powdered diketone (III) were added 50 c.c. of hydriodic acid (specific gravity 1·7), and the mixture was gently warmed for a short time. At first an oily mass formed at the surface of the liquid, but on heating and shaking the oil was converted into a solid. The flask was now cooled, and the contents were poured into an aqueous solution of sodium bisulphite, filtered, and the residue was washed with cold dilute sodium hydroxide and then with water. (A test portion was first examined in this way, and found to be almost insoluble in sodium hydroxide.) The product on crystallization from aqueous alcohol was obtained in fair yield as almost colourless plates, melting at 186°. Analysis gave the following results :—

0·1261 g. of the substance gave 0·3070 g. of CO_2 and 0·0624 g. of H_2O,
corresponding to C 66·4, H 5·5.
$C_{19}H_{18}O_6$ requires C 66·7, H. 5·3 %.

5 : 7 : 2′ : 4′-Tetramethoxyflavone gives a yellow solution with a blue fluorescence in strong sulphuric acid. Addition of a drop of ferric chloride to a solution of the compound in alcohol gives a brownish-green coloration.

5 : 7 : 2′ : 4′-Tetrahydroxyflavone (IV).

To the powdered tetramethoxyflavone (2 g.) or the benzoylacetophenone derivative (III) (2 g.) hydriodic acid (20 c.c.) of specific gravity 1·94 was

added, and the mixture was boiled under reflux for 5 hours. The product was poured with shaking into aqueous sodium bisulphite, allowed to remain at the room temperature for a short time, then filtered, washed with water, and dried. The reddish-yellow solid was washed with chloroform and crystallized from alcohol, when it was obtained in a pure condition. The yield of the pure product was small. Analysis gave the following results:—

0·1053 g. of the substance gave 0·2415 g. of CO_2 and 0·0309 g. of H_2O,

corresponding to C 62·55, H 3·3.
$C_{15}H_{10}O_6$ requires C 62·9, H 3·5 %.

5 : 7 : 2′ : 4′-Tetrahydroxyflavone is a crystalline powder consisting of bright-yellow plates, similar in appearance to the natural colouring matter, lotoflavin.

The following experiments were carried out with the natural and the synthetic compound, the results being very similar in each case:—

The substance was almost insoluble in water, chloroform, ether, or light petroleum. The solution in alcohol, aqueous sodium hydroxide, sodium carbonate, barium hydroxide, or borax, was bright yellow in colour. The solution in alcohol gave an orange-coloured precipitate with alcoholic lead acetate. Addition of a drop of ferric chloride solution to an alcoholic solution of the substance produced an olive-green coloration. Concentrated sulphuric acid gave a yellow solution with a greenish-blue fluorescence.

The melting point of the tetracetyl derivative of lotoflavin is given as 176°–178° by Dunstan and Henry (*loc. cit.*). Only a small quantity of the synthetic compound was available for acetylation, and an acetyl derivative of it (produced by the action of acetic anhydride and sodium acetate) was found to consist of small colourless plates (from alcohol), which melted, not sharply, in the neighbourhood of 200°. The amount obtained was, however, insufficient for analysis, and the difference in melting point of the two acetyl derivatives is not, therefore, decisive. Further experiments must be made on the acetylation as well as the methylation of the two substances, the natural and the synthetic, with a view to determining the cause of this possible discrepancy.

2 : 4 : 6 : 2′ : 4′-Pentamethoxybenzoylacetophenone (V).

This compound was obtained in the same way as the benzoylacetophenone derivative previously described (III). Phloroacetophenone trimethyl ether (5 g.), methyl 2 : 4-dimethoxybenzoate (7 g.), and finely divided sodium (0·9 g.) were employed, and the mixture was first heated to 100° for a short time, and then to 160°, the oily mass being shaken at intervals. At the end of 2 hours, as no further action was observed, the product was extracted with dilute sodium hydroxide and filtered. On acidification of the filtrate with 5 % acetic acid a white oily solid was precipitated. This was allowed to remain at the room temperature for 12 hours, when it was filtered, and the residue taken up with

alcohol. On crystallization from this solvent colourless plates, melting at 153°, were deposited. Analysis gave the following results:—

0·1719 g. of the substance gave 0·4010 g. of CO_2 and 0·0882 g. of H_2O,
corresponding to C 63·6, H 5·7.
$C_{20}H_{22}O_7$ requires C 64·2, H 5·9 %.

2 : 4 : 6 : 2′ : 4′-Pentamethoxybenzoylacetophenone is insoluble in water, slightly soluble in ether, readily soluble in hot alcohol, glacial acetic acid, or chloroform. The solution in sodium hydroxide is colourless, in concentrated sulphuric acid greenish-yellow with a blue-green fluorescence. The alcohol solution gives an olive coloration with a drop of ferric chloride solution. On shaking up an ethereal solution of the ketone with aqueous copper acetate a green copper derivative is precipitated. It is insoluble in ether, but may be recrystallized from benzene, in which it is moderately soluble.

7 : 2′ : 4′ : 6′-Tetramethoxyflavone.

This compound was produced by treatment of the ketone (V) with hydriodic acid of specific gravity 1·7 for a brief period, as in the preparation of the other tetramethoxyflavone. The product crystallized out from alcohol as colourless plates, melting at 171°, and gave the following results on analysis:—

0·1153 g. of the substance gave 0·2807 g. of CO_2 and 0·0570 g. of H_2O,
corresponding to C 66·4, H 5·5.
$C_{19}H_{18}O_6$ requires C 66·7, H 5·3 %.

A mixture of equal quantities of this substance and 5 : 7 : 2′ : 4′-tetramethoxyflavone melted at about 146°.

7 : 2′ : 4′ : 6′-Tetramethoxyflavone is slightly soluble in ether, readily soluble in alcohol, chloroform, or acetic acid. The solution in concentrated sulphuric acid is yellow, and exhibits a greenish-blue fluorescence; the alcohol solution gives a green coloration with a drop of ferric chloride.

7 : 2′ : 4′ : 6′-Tetrahydroxyflavone (VI).

This flavone was prepared by the action of hydriodic acid (specific gravity 1·94) on 2 : 4 : 6 : 2′ : 4′-pentamethoxybenzoylacetophenone (V) or on 7 : 2′ : 4′ : 6′-tetramethoxyflavone. The mixture was refluxed for 5 hours, and then poured into aqueous sodium bisulphite, after a short time filtered, washed with water and chloroform, and crystallized from alcohol. The pure substance consisted of minute yellow plates, which melted at about 240°, with darkening. The yield was small. The following results were obtained on analysis—

0·1627 g. of the substance gave 0·3736 g. of CO_2 and 0·0483 g. of H_2O,
corresponding to C 62·6, H 3·3.
$C_{15}H_{10}O_6$ requires C 62·9, H 3·5 %.

7 : 2′ : 4′ : 6′-Tetrahydroxyflavone is slightly soluble in light petroleum or chloroform, readily soluble in hot alcohol or glacial acetic acid. Its solution in alcohol, which is yellow in colour, gives a reddish precipitate with alcoholic lead acetate, and a brownish-green coloration with ferric chloride. In concentrated sulphuric acid the solution is yellow, and exhibits a greenish-blue fluorescence.

The acetyl derivative, produced by the action of acetic anhydride and fused sodium acetate, did not possess a sharp melting point. It crystallized from acetic acid in minute colourless leaflets, melting at about 230°.

Summary.

5 : 7 : 2′ : 4′-Tetrahydroxyflavone has been synthesized, and found to possess properties similar to those of the colouring matter of the *Lotus arabicus*, lotoflavin, thus supporting the constitution assigned to that substance.

Phloroacetophenone-4 : 6-dimethyl ether (I) was prepared from the corresponding 2 : 4 : 6-trimethyl ether by treating it with aluminium chloride, the trimethyl ether being obtained from phloroglucinol trimethyl ether by the action of acetyl chloride and ferric chloride.

Methyl 2 : 4-dimethoxybenzoate (II) was formed by the action of dimethyl sulphate on β-resorcylic acid.

The condensation of phloroacetophenone-4 : 6-dimethyl ether and methyl 2 : 4-dimethoxybenzoate in the presence of sodium gave 2-hydroxy-4 : 6 : 2′ : 4′-tetramethoxybenzoylacetophenone (III).

On treatment with hydriodic acid the diketone (III) was converted into 5 : 7 : 2′ : 4′-tetramethoxyflavone; and the last-named compound, or the diketone (III), by the further action of the same reagent, gave 5 : 7 : 2′ : 4′-tetrahydroxyflavone (IV).

The condensation of phloroacetophenone trimethyl ether in the same way with methyl 2 : 4-dimethoxybenzoate (II) produced 2 : 4 : 6 : 2′ : 4′-pentamethoxybenzoylacetophenone (V), which was changed into 7 : 2′ : 4′ : 6′-tetramethoxyflavone by the action of hydriodic acid. 7 : 2′ : 4′ : 6′-Tetrahydroxyflavone (VI) was obtained from the corresponding tetramethoxyflavone, or from the diketone (V) by the aid of the same reagent.

No. 10.

THE ESTIMATION OF DIPHENYLAMINE AND DIPHENYLNITROSAMINE IN THE PRESENCE OF THEIR DERIVATIVES.

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Diphenylamine is extensively employed as a stabiliser for nitrocellulose powders. Its useful purpose consists in absorbing the oxides and oxyacids of nitrogen which are liberated by the deteriorating powder. The diphenylamine thus prevents the accelerating action of these nitrogen compounds on the rate of decomposition of the nitrocellulose, and lengthens the life of the powder.

According to M. Buisson (Le Problème des Poudres), the diphenylamine absorbs the decomposition products of the nitrocellulose, and is itself converted into diphenylnitrosamine. This latter substance also exerts a stabilising influence, and is converted into more highly nitrated derivatives, which no longer possess, to a marked extent, the power of absorbing nitrous fumes. The amount of diphenylamine and diphenylnitrosamine remaining in the powder at any time may be regarded as an indication of its reserve of stability.

A method of estimating the "safe-period" of a powder has been suggested by M. Berger, of the Commission des Poudres de Versailles. The nitrocellulose powder is decomposed by boiling with dilute caustic soda, and the diphenylamine is then volatilised with steam, and estimated volumetrically in chloroform solution by means of bromine water. The diphenylamine is assumed to form a tetrabromo derivative. M. Berger states that the diphenylnitrosamine existing in the powder is converted by the caustic soda, in the presence of the products of the decomposition of the nitrocellulose, into diphenylamine, and thus added to the unchanged stabiliser. Two of the present authors, Ryan and Dunne, have, however, satisfied themselves that caustic soda alone did not prevent the diphenylnitrosamine from distilling as such.

Dreger (Chem. Zentralbl., 1909, **1**, p. 1507) suggested another method, in which, after the preliminary treatment with caustic soda, the diphenylamine was brominated in alcoholic solution, and the weight of the resulting bromo compound was ascertained. It was again assumed that only a tetrabromo derivative was formed.

Another method has been suggested by Ryan and Dunne. This method

consists in the extraction of the powder with alcohol, and the subsequent reduction of the extractive in alcoholic solution with stannous chloride and hydrochloric acid. The alcohol is removed from the mixture, which is then distilled in a current of steam. The diphenylamine in the distillate is extracted with chloroform, and estimated volumetrically with bromine water. By this treatment it is claimed that the diphenylnitrosamine is quantitatively converted into diphenylamine, which is easily volatile with steam. The other nitro derivatives of the stabiliser, such as 4-nitrodiphenylamine and 4-nitrodiphenylnitrosamine, are converted into reduction compounds, the hydrochlorides of which do not distil in a current of steam. It was, therefore, possible to isolate the diphenylamine which existed as such in the powder, together with the amount which was formed by the reduction of the nitrosamine. In this manner it is claimed that accurate results may be obtained for the estimation of the total reserve of stability in the powder. The use of aqueous bromine as a volumetric solution has been investigated by Ryan and Keane. The action of bromine water on diphenylamine and on some of its derivatives has been studied, and we have satisfied ourselves that the use of the aqueous solution is attended by serious difficulties. Thus, the apparent absorption of bromine was found to vary with the light conditions. It was also dependent on the concentration of the bromine water and the excess of the solution employed, as a certain amount of the bromine is lost by volatilisation in each experiment. By treating diphenylamine with an aqueous solution of bromine in indirect sunlight at 15° C. for half an hour, it was found that the amount of bromine absorbed corresponded approximately to the formation of a tribromo derivative. When the experiment was carried out in the absence of light, the bromine absorption corresponded to the formation of a dibromo compound. In neither case was the result sufficiently definite to be of practical value. Similar experiments were performed, using diphenylnitrosamine, 4-nitrodiphenylamine, and other nitro derivatives of the stabiliser. The results of the experiments, however, were variable and indefinite. This may be attributed partly to the appreciable and uncertain loss of bromine when filling the burette, and again during the experiment.

To reduce these errors, it was considered that a chloroform solution of bromine might with advantage be substituted for the aqueous solution. In favour of using chloroform as a solvent for the bromine, it may be mentioned that it is possible to work with stronger solutions than in the case where the aqueous solution is used. This renders one filling of the burette sufficient for an experiment, and reduces somewhat the loss which occurs in using bromine water when two or more fillings of the burette may be necessary. Again, it was found that by using a solution of bromine in chloroform, the apparent absorption of bromine in the experiment did not vary very much with varying light conditions. It was found that the bromine absorption in the case of diphenylamine corresponded to the formation of a tetrabromo compound, and in the case of 4-nitrodiphenylamine to a tribromo body. Similarly, the amount of bromine

absorbed by diphenylnitrosamine corresponded to the formation of a dibromo derivative, and in the case of 4-nitrodiphenylnitrosamine and 2·4-dinitrodiphenylamine to a monobromo compound. In the case of 2·10-dinitrodiphenylnitrosamine, 2·4·8·10-tetranitrodiphenylamine, and hexanitrodiphenylamine there was no appreciable absorption of bromine. It is worthy of note that the absorption of bromine by the different nitro derivatives of diphenylamine appreciably decreases as the nitrogen content of the compounds becomes greater.

The modification of the method proposed by Ryan and Dunne, by the substitution of a chloroform for an aqueous solution of bromine, would lead to more satisfactory results. Thus, the nitrocellulose powder could be extracted with alcohol, and the extractive reduced with stannous chloride and hydrochloric acid. On passing a current of steam through the reduced mixture, a definite amount of diphenylamine distils, and can be extracted with chloroform, and then estimated volumetrically by means of a solution of bromine in chloroform.

The action of a chloroform solution of bromine on mixtures of two nitro derivatives of diphenylamine was next examined. In these experiments it was found that the apparent absorption of bromine was greater than the theoretical quantity, especially when diphenylnitrosamine was present in the mixture. The theoretical amount of bromine was calculated from the results of the action of the same solution of bromine on the individual nitro compounds. The higher value of the apparent bromine absorption may be ascribed to concurrent reactions which take place, and are due presumably to the nitroso group. Nevertheless, it is strange that the bromine absorbed by diphenylnitrosamine should be different when the compound is used alone, and in mixtures with diphenylamine and other nitro derivatives of the stabiliser. It was noticed that if one-tenth of the apparent absorption of bromine was deducted from the experimental value, the amended figure agrees fairly well with the theoretical amount. Thus, with 0·1712 gram. of diphenylamine and 0·1648 gram. of diphenylnitrosamine, the apparent absorption of bromine corresponded to 128·18 c.c. of a deci-normal solution. On deducting one-tenth of this value, the amended figure becomes 115·36 c.c., whilst the theoretical absorption was 114·33 c.c.

The absorption of bromine by mixtures of diphenylamine and its nitro derivates appears to be normal. The bromination proceeds as if the individual substances were being used, provided that one-tenth of the apparent absorption of bromine be deducted from the experimental value.

The following method of estimating the amount of diphenylamine and of its lower nitro derivatives would prove very convenient if it was found to be practicable. The nitrocellulose powder could be extracted with chloroform for a definite period in a Soxhlet apparatus. The chloroform solution of the extractive could then be concentrated to about ten cubic centimetres, and treated directly with a chloroform solution of bromine. The apparent absorption of bromine could then be compared with empirically fixed standards. The

absorption of bromine is greatest in the case of diphenylamine and of its lower nitro compounds, and it will be remembered that the reserve of stability of a powder is indicated by the amount of the stabiliser and of its nitrosamine which are present at a given time. The presence of 4-nitrodiphenylamine and of 2·4-dinitrodiphenylamine would, however, interfere to a certain extent with the method, as they both absorb bromine. By submitting the chloroform extractive to an exhaustive chemical analysis, it might be possible to fix a standard for the bromine absorption, and thus determine in a ready manner whether the nitrocellulose powder was suitable for further magazine storage.

Experimental.

I.—*DISTILLATION IN A CURRENT OF STEAM.*

Diphenylamine, diphenylnitrosamine, 4-nitro-diphenylamine, 4-nitro-diphenylnitrosamine, crude dinitro-diphenylnitrosamine, 2·4·8·10-tetranitro-diphenylamine and 2·4·6·8·10·12-hexanitro-diphenylamine were subjected separately to distillation in a current of steam, under conditions which were alike in all the experiments.

A.—*Steam at 100° C.*

1. *Diphenylamine.*—1 g. of diphenylamine was placed in a litre flask connected with a Liebig's condenser and with a source of steam. The steam was generated at the ordinary pressure. About 92 % of the diphenylamine distilled with the steam in one hour, and the remaining 8 % shortly afterwards. The diphenylamine in the distillate was estimated by extraction with chloroform and direct weighing.

2. *Diphenylnitrosamine.*—In the case of diphenylnitrosamine, although about 80 % distilled with the steam during the first hour, the distillation was incomplete even after five hours, a greenish decomposition product remaining in the flask.

3. *4-Nitro-Diphenylamine.*—4-Nitro-diphenylamine was only very slightly volatile with the steam. The amount which distilled was merely sufficient to impart a yellow colour to the condensed water.

4. *4-Nitro-Diphenylnitrosamine.*—Like its corresponding amine, 4-nitro-diphenylnitrosamine was but slightly volatile with the steam.

5. *Dinitro-Diphenylnitrosamine.*—A crude mixture of 2·10- and 4·10-dinitro-diphenylnitrosamines was, like the mono-nitro compound, but very slightly volatile with the steam.

6. *Tetranitro-Diphenylamine.* — 2·4·8·10-Tetranitro-diphenylamine did not distil with the steam, the condensed water being quite colourless.

7. *Hexanitro-Diphenylamine.*—Hexanitro-diphenylamine was scarcely volatile with the steam, the condensed water having but a very faint yellow coloration, due probably to some impurity in the hexanitro-diphenylamine.

8. *Diphenylamine with Diphenylnitrosamine.* — A mixture of 0·5 g. diphenylamine and 0·5 g. diphenylnitrosamine was distilled in a current of

steam. The main portion of the mixture distilled within 2 hours from the flask, in which a greenish decomposition product remained.

B.—*Steam at 250° C.*

1. *Diphenylamine.*—In presence of the superheated steam, diphenylamine distilled rapidly and completely.

2. *Diphenylnitrosamine.*—Diphenylnitrosamine distilled with the superheated steam, but the amount of the dark green tarry decomposition product remaining in the flask was greater than that got when the nitrosamine was distilled in a current of steam at 100° C.

3. *4-Nitro-Diphenylamine.*—4-Nitro-diphenylamine was slightly volatile with the superheated steam.

4. *4-Nitro-Diphenylnitrosamine.*—This substance, like 4-nitro-diphenylamine, is not very volatile with the superheated steam. After several hours' distillation, about one-half of the nitrosamine had distilled with the steam.

C.—*From an Acid Solution.*

1. *Diphenylamine.*—0·98 g. of diphenylamine was distilled with steam at 100° C. in the presence of 10 c.c. of 25 % hydrochloric acid; 0·9 g. distilled over in one hour, and the remainder shortly afterwards.

2. *Diphenylnitrosamine.*—In the presence of 10 c.c. of 25 % hydrochloric acid about two-thirds of the unchanged diphenylnitrosamine distilled with the steam, and a dark green tarry decomposition product remained in the flask.

D.—*From an Alkaline Solution.*

1. *Diphenylnitrosamine.*—About 0·3 g. of diphenylnitrosamine was treated in a litre flask with 500 c.c. of 6 % caustic soda. The mixture was heated on a sandbath until 300 c.c. of condensed liquid had collected in the receiver. During this process approximately 75 % of the nitrosamine distilled unchanged with the steam.

II.—*QUANTITATIVE ACTION OF BROMINE ON DIPHENYLAMINE AND SOME OF ITS DERIVATIVES IN CHLOROFORM SOLUTION.*

Diphenylamine, diphenylnitrosamine, 4-nitro-diphenylamine, 4-nitro-diphenylnitrosamine, and crude dinitrodiphenylnitrosamine, in chloroform solution, were each treated separately with a known volume of bromine water; subsequently mixtures of two or more of these were treated similarly. To determine the total quantity of bromine introduced, 20 c.c. of the bromine water were added from a burette to a potassium iodide solution and titrated against standard sodium thiosulphate. The bromine was usually allowed half-an-hour to form bromo derivatives, and at the end of that time a solution of potassium iodide was added, the iodine set free being estimated

by addition of standard sodium thiosulphate. The amount of bromine absorbed in the formation of bromo derivatives and of hydrobromic acid was then calculated.

1. *Diphenylamine.*—Weighed quantities, 0·2 g. approximately, of diphenylamine dissolved in 30 c.c. of chloroform were treated with bromine water of various strengths for different periods of time. The amount of bromine absorbed, stated as cubic centimetres of a decinormal solution, was determined in each case, and compared with the amount (hereafter referred to as the "theoretical" amount) that should have been absorbed were all the diphenylamine converted into a tetrabromo derivative. The results of the various experiments are shown in tabulated form in Table A.

TABLE A.

Strength of bromine water.	Time of bromination in minutes.	Molecular amounts of bromine per one molecular amount of diphenylamine.	Number of c.c. of decinormal bromine		Percentage divergency.
			required theoretically.	actually absorbed.	
3·514 $\frac{N}{10}$	15	6	94·7	94·7	0
3·514 ,,	30	6	98·1	96·8	− 1
3·514 ,,	30	8	48·8	50·2	+ 3
3·514 ,,	30	4·8	93·8	93·5	− 0·5
2·464 ,,	30	5·3	83·8	86·8	+ 4
0·899 ,,	30	6	94·7	97·2	+ 3
0·899 ,,	30	4·8	95·5	99·8	+ 4
0·899 ,,	45	4·4	98·6	105·2	+ 6
0·899 ,,	60	4·8	100·4	105·8	+ 5
0·876 ,,	45	4·4	79·7	77	− 3
0·876 ,,	60	4·6	107·0	112·9	+ 5
0·869 ,,	30	4·4	109	103·1	− 5
0·869 ,,	30	4·8	106·5	103·4	− 2
0·271 ,,	90	4·2	104·9	105·8	+ 1

In the last column is given, in each case, the difference between the number of c.c. of bromine actually absorbed and the number theoretically required, stated as a percentage of the latter number. Thus, the figures in this column would correspond to percentage errors if the above method were employed for the estimation of diphenylamine. In the first four experiments the strength of

the bromine was taken as the mean of its strengths determined immediately before and after addition to the diphenylamine solution; in all the other cases the strength of the bromine was that determined immediately after the addition. Whilst there are indications that the amount of bromine absorbed depends on the time of bromination and the excess of bromine present, no definite conclusions can be drawn from Table A, as the results are too inconsistent for accurate estimations of diphenylamine.

2. *Diphenylnitrosamine.*—In the case of diphenylnitrosamine, treated similarly to the diphenylamine for half an hour, the amount of bromine absorbed varied from 15 to 20 % in excess of the amount required for the formation of a tetrabromo derivative.

(*a*) In one experiment 0·0988 g. of diphenylnitrosamine, theoretically requiring 39·9 c.c. of decinormal bromine, absorbed 46·9 c.c.

(*b*) In a second experiment 0·2656 g. of diphenylnitrosamine, requiring 107·3 c.c. of decinormal bromine, absorbed 128 c.c.

3. *4-Nitro-Diphenylamine.*—In chloroform solution 0·2376 g. of 4-Nitro-diphenylamine absorbed 5·3 c.c. of deci-normal bromine, corresponding to 25 % of the amount required for the formation of a mono-bromo derivative.

4. *4-Nitro-Diphenylnitrosamine.*—0·2029 g. of 4-Nitro-diphenylnitrosamine absorbed 1·7 c.c. of deci-normal bromine.

5. *Dinitro-Diphenylnitrosamine.*—0·2 g. of crude 2·10- and 4·10-dinitro-diphenylnitrosamine absorbed no bromine.

6. *Diphenylamine and Diphenylnitrosamine.*—0·0649 g. of diphenylamine and 0·0984 g. of diphenylnitrosamine absorbed 78·1 c.c. of deci-normal bromine. The formation of a tetra-bromo derivative from each would require 70·5 c.c.

7. *Diphenylamine and 4-Nitro-Diphenylamine.*—0·2313 g. of diphenylamine with 0·2559 g. of 4-nitro-diphenylamine absorbed 115·6 c.c. of deci-normal bromine, 109·5 c.c. being required theoretically by the diphenylamine.

8. *Diphenylamine and 4-Nitro-Diphenylnitrosamine.*—0·2249 g. of diphenylamine and 0·166 g. of 4-Nitro-diphenylnitrosamine absorbed 113·8 c.c. of deci-normal bromine, the diphenylamine alone requiring theoretically 106·5 c.c.

9. *Diphenylamine, 4-Nitro-Diphenylnitrosamine, and Dinitro-Diphenylnitrosamine.*—0·195 g. of diphenylamine with 0·1 g. of 4-Nitro-diphenylnitrosamine and 0·05 g. of crude 2·10- and 4·10-dinitro-diphenylnitrosamine absorbed 94·6 c.c. of deci-normal bromine, the diphenylamine alone requiring theoretically 92·3 c.c.

A consideration of Table A shows that no reliance could be placed on the method described in A as a consistent means of estimating the amount of diphenylamine present in its chloroform solution. Better results were obtained by some slight modifications, which had the effect of making the method more

similar to that actually carried out on the N/c powder, as recommended by M. Berger.

10. *Diphenylamine.*—0·2 g. of diphenylamine was weighed into a litre flask, dissolved in chloroform, covered with 300 c.c. of water, and then 40 c.c. of bromine water was added from a burette. The flask was corked, and shaken every five minutes. Meanwhile, the remaining 10 c.c. of bromine were added to a solution of potassium iodide, and the strength of the bromine determined. At the end of half an hour the excess of bromine in the flask was estimated by the usual method. The amount of bromine absorbed was 1 % in excess of the amount required for the complete formation of a tetrabromo derivative of diphenylamine. With larger excesses of bromine present the divergency increased to 2 and 3 %, as may be seen in Table B, where the results of three separate experiments are recorded.

11. *Diphenylnitrosamine.*—Diphenylnitrosamine was treated similarly to the diphenylamine in (1), but here the divergency between the amount of bromine absorbed and the theoretical amount required for the formation of a tetrabromo derivative was as high as 10 and 12 % in two separate experiments. The results of these experiments for diphenylamine and diphenylnitrosamine are recorded underneath in Table B.

TABLE B.

Diphenylamine.

Molecules of bromine per one molecule of substance.	Number of c.c. of decinormal bromine		Percentage Divergency.
	required theoretically.	actually absorbed.	
5·2	100·0	101·0	+ 1
5·7	62·8	63·7	+ 1·4
7·1	77·3	80·1	+ 3·6
	Diphenylnitrosamine.		
5·1	100·5	110·5	+ 10
5·4	99·9	112·4	+ 12·5

III.—*EFFECT OF VARYING THE EXPERIMENTAL CONDITIONS ON THE ACTION OF AN AQUEOUS SOLUTION OF BROMINE ON DIPHENYLAMINE.*

A small quantity of diphenylamine (about 0·2 g.) was introduced into a conical flask containing about 5 c.c. of chloroform. 100 c.c. of bromine water (0·2 N) were quickly added to the contents of the flask, which was then immersed in a water-bath at 15° C. and removed to a dark cupboard. After half an hour the flask was withdrawn, and 5 g. of potassium iodide were added to its contents. An excess of decinormal sodium thiosulphate was then added, until the violet colour in the chloroform layer became discharged. After adding a few drops of starch solution, the excess of thiosulphate was estimated by means of a standard solution of iodine.

This method of finding the amount of iodine liberated by the excess of bromine used was found to give more satisfactory results than the direct estimation of the iodine by means of thiosulphate.

The action of bromine water on diphenylamine was also examined in indirect sunlight, and the results of the experiments are given below:—

Amount of diphenlyamine.	Degree of bromination.	Absorption of bromine		Experimental conditions.
		Theoretical.	Experimental.	
0·2050 g.	Tribromo.	75·78 c.c. of $\frac{N}{10}$	76·85 c.c.	Indirect sunlight.
0·2075 g.	Tribromo.	76·67 „ „	72·75 c.c.	Laboratory temperature.
0·1983 g.	Dibromo.	46·94 „ „	45·26 c.c.	In the dark, 15° C.

The action of bromine water, then, on diphenylamine varies considerably with varying light conditions.

IV.—*EFFECT OF VARYING THE EXPERIMENTAL CONDITIONS ON THE ACTION OF AN AQUEOUS SOLUTION OF BROMINE ON NITRO DERIVATIVES OF DIPHENYLAMINE.*

In the following experiments, 0·15 to 0·25 g. of different nitro derivatives of diphenylamine were treated under varying conditions with bromine water. The results which were obtained are given below. In the third column, the

theoretical absorption of bromine is given, assuming the degree of bromination set down in the second column :—

Substance.	Degree of bromination.	Expressed in terms of $\frac{N}{10}$ bromine water. Theoretical absorption of bromine.	Actual absorption.	Experimental conditions.
Diphenylnitrosamine	Dibromo.	41·71 c.c.	44·05 c.c.	Indirect sunlight, 15° C.
,,	,,	45·38 c.c.	52·02 c.c.	,, ,, ,,
,,	,,	44·3 c.c.	52·31 c.c.	,, ,, ,,
Diphenylnitrosamine.	Monobromo.	26·06 c.c.	20·51 c.c.	In the dark, 15° C.
,,	,,	21·74 c.c.	20 26 c.c.	,,
,,	,,	24·18 c.c.	26·52 c.c.	,, ,,
4-nitrodiphenylamine.	Monobromo.	13·49 c.c.	19·01 c.c.	In the dark, 15° C.
,,	,,	9·10 c.c.	16·87 c.c.	Indirect sunlight, 15° C.
2·4-dinitro-diphenylamine.	Monobromo.	16·00 c.c.	23·33 c.c.	In the dark, 15° C.
,,	,,	13·13 c.c.	15·29 c.c.	,, ,,
4-nitro-diphenylnitrosamine.	None.	—	3·13 c.c.	In the dark, 15° C.
2·10-dinitro-diphenylnitrosamine.	,,	—	3·54 c.c.	,, ,,
2·4·8·10-tetranitrodiphenylamine.	,,	—	3·93 c.c.	,, ,,
Hexanitrodiphenylamine.	,,	—	3·95 c.c.	,, ,,

From the foregoing figures, the varying nature of the results which were obtained under different experimental conditions may again be seen. The reasons for these indefinite results are to be found in the many sources of error which attend the use of bromine water as a volumetric solution. Firstly, appreciable losses of bromine occur in transferring its aqueous solution from the storage bottle to the burette, and again from the burette to the conical flask. Since a certain excess of bromine must be used in each experiment, it follows that a considerable loss must ensue, and that this loss varies according to the excess used in the experiment. Again, the apparent absorption of bromine varies considerably with the light conditions. In Dunne's experiments, the bromination was allowed to proceed for an hour in daylight, and at laboratory temperatures. Under these conditions, he found that the amount of bromine absorbed by diphenylnitrosamine was 20 % in excess of the quantity

required for the formation of a tetrabromo compound. From a qualitative and quantitative examination of the brominated product, Dunne showed that the absorption of bromine should not have been in excess of the amount required for the formation of a tetrabromo derivative. It thus appears that the disadvantages attending the use of an aqueous solution of bromine render it unsuitable for the volumetric estimation of diphenylamine or its derivatives.

V.—*EXAMINATION OF THE CHANGE IN STRENGTH OF A SOLUTION OF BROMINE IN CHLOROFORM.*

In examining the action of a chloroform solution of bromine on different nitro derivatives of diphenylamine, it was noticed that the strength of the solution did not alter very considerably over comparatively long intervals of time. Thus, a semi-normal solution of bromine only lost 12 % of its strength on being repeatedly used for sixteen days.

Day of Experiment . .	1st	7th	8th	13th	14th	15th	16th
Strength of Bromine . .	0·5875N	0·5505N	0·5505N	0·5425N	0·533N	0·5253N	0·5152N

VI.—*ACTION OF A SOLUTION OF BROMINE IN CHLOROFORM ON DIPHENYLAMINE.*

Forty c.c. of a solution of bromine were added to a solution of 0·2 g. (or 0·3 g.) of diphenylamine in 5 c.c. of chloroform contained in a clean conical flask.

The flask was then stoppered, and allowed to remain for half-an-hour under varied experimental conditions. After this time, 10 c.c. of a strong aqueous solution of potassium iodide were added to the contents of the flask, and then an excess of a decinormal solution of sodium thiosulphate. The excess of the thiosulphate used was then estimated by means of a standard solution of iodine. The results are given in tabular form.

Amount of diphenylamine.	Absorption of bromine (expressed in c.cs. of $\frac{N}{10}$ solution.)		Experimental conditions.
	Theoretical.	Experimental.	
	(For the formation of a tetrabromo compound.)		
0·2852 g.	135·0 c.c.	134·94 c.c.	Indirect sunlight.
0·3020 „	143·0 c.c.	142·66 c.c.	Laboratory temperature.
0·2510 „	123·82 c.c.	123·42 c.c.	In the dark, 15° C.

From these results, it would appear that bromine in chloroform solution reacts with diphenylamine to form a tetrabromo compound, and the absorption of bromine does not vary very much under different light conditions.

VII.—*ACTION OF BROMINE IN CHLOROFORM SOLUTION ON NITRO DERIVATIVES OF DIPHENYLAMINE.*

In examining the action of a chloroform solution of bromine on the nitro derivatives of diphenylamine, a small quantity (about 0·2 g.) of the different substances was treated in a manner similar to that adopted with diphenylamine, as described in the foregoing section.

In the following table the degree of bromination which each substance is supposed to undergo is first given, and then the corresponding theoretical absorption of bromine :—

Substance.	Degree of bromination.	Absorption of bromine (expressed in c.c. of $\frac{N}{10}$ solution).		Experimental conditions.
		Theoretical.	Actual.	
Diphenylnitrosamine.	Dibromo	60·81 c.c.	59·72 c.c.	Indirect sunlight.
,,	,,	61·43 c.c.	60·76 c.c.	Laboratory temperature.
,,	,,	50·98 c.c.	48·78 c.c.	In the dark.
,,	,,	52·23 c.c.	48·47 c.c.	
,,	,,	43·09 c.c.	42·54 c.c.	Laboratory temperature.
4-nitrodiphenylamine.	Tribromo.	34·18 c.c.	36·05 c.c.	,,
,,	,,	24·88 c.c.	27·83 c.c.	,,
4-nitrodiphenylnitrosamine.	Monobromo.	17·07 c.c.	19·53 c.c.	,,
2·4-dinitrodiphenylamine.	Monobromo.	19·80 c.c.	19·03 c.c.	,,
2·10-dinitrodiphenylnitrosamine.	None.	—	0·364 c.c.	,,
2·4·8·10-tetranitrodiphenylamine.	,,	—	1·50 c.c.	,,
2·4·6·8·10·12-hexanitrodiphenylamine.	,,	—	0·65 c.c.	,,

From the above experiments, which were performed under varying conditions, it appears that the amounts of bromine absorbed by the different compounds are fairly constant. It is also worthy of note that, according as the percentage of nitrogen increases in the nitro derivatives of diphenylamine, the absorption of bromine falls off correspondingly.

VIII.—*ACTION OF A CHLOROFORM SOLUTION OF BROMINE ON MIXTURES OF DIFFERENT NITRO DERIVATIVES OF DIPHENYLAMINE.*

In the following experiments small quantities of different pairs of compounds, consisting of diphenylamine and its nitro derivatives, were treated with a chloroform solution of bromine. The apparent absorption of bromine was ascertained in a similar manner to that described in the previous sections. In deducing the theoretical amounts of bromine absorbed, it was assumed that each nitro derivative formed the same bromo compound, as set out in the previous section (VII).

Mixture.	Bromine absorbed (expressed in c.c. of $\frac{N}{10}$ solution).			
	Apparent.	Corrected.	Theoretical.	
0·1529 g. Diphenylamine ... ... 0·0710 „ Diphenylnitrosamine	93·44 c.c.	84·1 c.c.	Diphenylamine ... ... Diphenylnitrosamine	72·39 c.c. 14·34 c.c.
			Total	86·73 c.c.
0·1414 g. Diphenylamine ... ... 0·1528 „ Diphenylnitrosamine	107·55 c.c.	96·79 c.c.	Diphenylamine ... ... Diphenylnitrosamine	66·93 c.c. 30·82 c.c.
			Total	97·75 c.c.
0·1712 g. Diphenylamine ... ... 0·1648 „ Diphenylnitrosamine	128·18 c.c.	115·36 c.c.	Diphenylamine ... ... Diphenylnitrosamine	81·04 c.c. 33·29 c.c.
			Total	114·33 c.c.
0·1014 g. Diphenylamine ... ... 0·0993 „ 4-nitrodiphenylnitrosamine ...	54·11 c.c.	48·7 c.c.	Diphenylamine 4-nitrodiphenylnitrosamine	48·00 c.c. 5·67 c.c.
			Total	53·67 c.c.
0·0980 g. Diphenylamine ... ... 0·1032 „ 2·4-dinitrodiphenylamine ...	56·45 c.c.	50·81 c.c.	Diphenylamine ... ... 2·4-dinitrodiphenylamine	46·39 c.c. 7·97 c.c.
			Total	54·36 c.c.
0·1077 g. Diphenylamine ... ... 0·1061 „ 2·10-dinitrodiphenylnitrosamine	50·50 c.c.	45·45 c.c.	Diphenylamine ... ... 2·10-dinitrodiphenylnitrosamine ...	50·9 c.c. 0·0 c.c.
			Total	50·9 c.c.
0·1000 g. Diphenylamine ... ... 0·1038 „ 4-nitrodiphenylamine	74·07 c.c.	66·67 c.c.	Diphenylamine 4-nitrodiphenylamine	47·34 c.c. 19·4 c.c.
			Total	66·74 c.c.
0·1240 g. Diphenylnitrosamine ... ... 0·1996 „ 4-nitrodiphenylnitrosamine ...	45·29 c.c.	40·77 c.c.	Diphenylnitrosamine 4-nitrodiphenylnitrosamine	25·05 c.c. 16·15 c.c.
			Total	41·20 c.c.
0·1430 g. Diphenylnitrosamine ... ... 0·1000 „ 2·10-dinitrodiphenylnitrosamine	31·25 c.c.	28·13 c.c.	Diphenylnitrosamine ... ... 2·10-dinitrodiphenylnitrosamine ...	28·28 c.c. 0·0 c.c.
			Total	28 28 c.c.

The above experiments were conducted in indirect sunlight and at laboratory temperatures.

The theoretical and experimental amounts of bromine absorbed agreed rather well, except when diphenylnitrosamine was present in the mixture. In these cases, it was noticed that, by deducting one-tenth of the experimental bromine absorption, the corrected figures (column 3) were in much better agreement with the theoretical values. This deduction is given in every case, and, on the whole, there appears to be a fairly close agreement between the corrected absorptions of bromine and the theoretical values:—

IX.—*SEPARATION OF DIPHENYLAMINE AND DIPHENYLNITROSAMINE BY MEANS OF STANNOUS CHLORIDE AND HYDROCHLORIC ACID.*

When diphenylamine is distilled with steam in the presence of diphenylnitrosamine and 4-nitro-diphenylamine, from 80 to 90 % of the nitrosamine and a very small quantity of the 4-nitro-diphenylamine distil over with the diphenylamine. In a volumetric method, as described above in Section II, the amount of diphenylnitrosamine found in the distillate would be approximately 10 % in excess of the actual amount present. This would tend to counterbalance the error introduced through the non-volatilisation of portion of the nitrosamine during the steam distillation. The presence of the 4-nitro-diphenylamine interferes with the accurate estimation of the diphenylamine owing to a slight absorption of the bromine by the 4-nitro body. With a view to removing this source of error, the effect of stannous chloride and hydrochloric acid on diphenylnitrosamine and on 4-nitro-diphenylamine was examined.

1. *Diphenylnitrosamine.*—1 g. of diphenylnitrosamine was dissolved in alcohol, and treated in the cold with a solution of 8 g. of stannous chloride in 20 c.c. of hydrochloric acid. The mixture was warmed gently for some time, and distilled with steam, the alcohol being distilled off first. A white solid, resembling diphenylamine, distilled over, and there was a complete absence of any yellow coloration. On extraction of the distillate with chloroform and evaporation of the solvent, a slightly brownish solid was obtained. It melted between 51–53° C., weighed 0·83 g., and gave with sulphuric acid a colourless solution, which assumed a deep blue colour on addition of one drop of crude nitric acid. Since 1 g. of diphenylnitrosamine is equivalent to 0·8536 g. of diphenylamine, the diphenylnitrosamine must have been converted into, and recovered nearly quantitatively as diphenylamine.

2. *4-Nitro-Diphenylamine.*—4-Nitro-diphenylamine was reduced in alcoholic solution by the action of stannous chloride and hydrochloric acid, and it was found that the 4-amino-diphenylamine hydrochloride thus formed did not distil with steam.

3. In order to investigate the foregoing actions more accurately, diphenylnitrosamine alone, a mixture of diphenylamine with diphenylnitrosamine, and a mixture of diphenylamine with 4-nitro-diphenylamine were treated with stannous chloride and hydrochloric acid, as described above in (1), in the case of diphenylnitrosamine. A total weight of not more than 0·25 g. of diphenylamine, plus diphenylnitrosamine, was employed in each case, and the steam distillation was stopped when about 300 c.c. of water had condensed in the receiving flask. The condenser was well washed with chloroform, and the washings added to the receiving flask. The distillate was treated with bromine water, as in B, and the following are the results of the experiments:—

(*a*) *Diphenylnitrosamine.*—The number of c.c. of deci-normal bromine added was 123·4, the number required theoretically was 100·3, and the number actually absorbed was 101·7.

(*b*) *Diphenylamine with Diphenylnitrosamine.*—The number of c.c. of deci-normal bromine added was 116·2, the number required theoretically was 88·3, and the number actually absorbed was 89·8.

(*c*) *Diphenylamine and 4-Nitro-Diphenylamine.*—The number of c.c. of deci-normal bromine added was 128·7, the number required theoretically was 95·3, and the number actually absorbed was 96·2.

X.—*QUANTITATIVE ACTION OF BROMINE ON DIPHENYLAMINE AND SOME OF ITS DERIVATIVES IN ALCOHOLIC SOLUTION.*

Weighed quantities of diphenylamine, diphenylnitrosamine, 4-nitro-diphenylamine, and the crude mixture of 2·10- and 4·10-dinitro-diphenylnitrosamine were mixed separately with 20 to 30 c.c. of alcohol, and a slight excess of bromine was added slowly from a dropping funnel. The nitro compounds were only partially soluble in the cold alcohol. The mixtures were allowed to stand for half an hour, then about 150 c.c. of water was added to each, and the liquids were evaporated to half their volume. The yellow bromo compounds were collected, dried, and weighed.

1. *Diphenylamine.*—(*a*) 0·2481 g. of diphenylamine gave 0·6881 g. of a bromo compound. If tetrabromo-diphenylamine were formed quantitatively, its weight would be 0·7112 g.

(*b*) 0·2142 g. of diphenylamine gave 0·5918 g. of a bromo compound. If tetrabromo-diphenylamine were formed quantitatively, its weight would be 0·6140 g.

(*c*) 0·1765 g. of diphenylamine gave 0·4875 g. of a bromo compound. If tetrabromo-diphenylamine were formed quantitatively, its weight would be 0·5059 g.

2. *Diphenylnitrosamine.*—(*a*) 0·2341 g. of diphenylnitrosamine gave 0·5698 g. of a bromo-compound. If tetrabromo-diphenylamine were formed quantitatively, its weight would be 0·5728 g.

(*b*) 0·2690 g. of diphenylnitrosamine gave 0·6544 g. of a bromo compound. If tetrabromo-diphenylamine were formed quantitatively, its weight would be 0·6582 g.

3. *4-Nitro-Diphenylamine.*—(*a*) 0·1356 g. of 4-nitro-diphenylamine gave 0·2467 g. of a bromo compound, which corresponds to the addition of 172 g. of bromine to the gram molecular weight of 4-nitro-diphenylamine.

(*b*) 0·1421 g. of 4-nitro-diphenylamine gave 0·2620 g. of a bromo compound, which corresponds to the addition of 181 g. of bromine to the gram molecular weight of 4-nitro-diphenylamine.

4. *Dinitro-Diphenylnitrosamine.*—0·1866 g. of crude 2·10- and 4·10-dinitro-diphenylnitrosamine gave 0·2118 g. of a bromo compound, which corresponds to the addition of 39 g. of bromine to the gram molecular weight of dinitro-diphenylnitrosamine.

By repeated recrystallisations from chloroform, the magenta-coloured compound obtained as above from diphenylamine, and the yellow compound from diphenylnitrosamine, both gave white crystals of tetrabromo diphenylamine melting at 187° C.

The compound formed from 4-nitro-diphenylamine on recrystallisation from chloroform gave a bright yellow solid, which melted at 216° C., and was identical with the dibromo-4-nitro-diphenylamine obtained by the action of bromine in chloroform solution on 4-nitro-diphenylamine. (Proc. R.I.A., **34**, B. 13, p. 222.)

No. 11.

THE ACTION OF AROMATIC AMINES ON NITRIC ESTERS.

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Introduction.

It has long been known that amines often accelerate greatly the speed of the decomposition of a nitric ester. The variation in the speed of the decomposition appears to depend both on the ester and on the amine. In certain cases, as in that of a mixture of nitrocotton and benzylamine, the speed may be accelerated so much that the mixture inflames.

One would naturally expect that the effect of the amine on the speed of decomposition of the ester would vary with the affinity constant of the amine base. In a somewhat analogous phenomenon, aminolysis, or the decomposition of a salt of an amine by a basic anhydrous solvent, the aminolytic constants of the basic solvents do not always vary, however, in the same order as their affinity constants (Goldschmidt and Salcher, Zeit. phys. Chem. (1899), **29**, pp. 89–118).

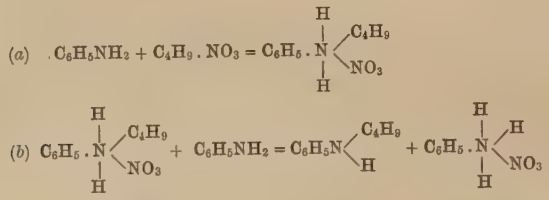
As the effect of an amine on the speed of decomposition of a nitric ester does not appear to vary in the same way as either the affinity constant or the aminolytic constant of the amine, it is difficult to interpret the phenomenon.

Farmer (Jour. Chem. Soc. (1920), p. 817) considered the decomposition of the nitric ester as an internal oxidation, facilitated by the presence of the amine.

Since, however, it appeared possible that the variation in the speed of the decomposition of the nitric ester might be due to a greater or lesser tendency of the nitric ester to nitrate the base, the experiments described below were conducted with a view to determining in how far nitric esters act as nitrating agents towards various aromatic amines.

In these experiments it was found that primary amines, such as aniline, *o*- and *p*-toluidine, and *m*-xylidine, interact with the nitric esters of ethyl, butyl, and amyl alcohols to form the nitrate of the amine base, and, in those cases which were examined in detail, the alkyl derivative of the amine. Thus, from

the products of the interaction of aniline and butyl nitrate we were able to isolate aniline nitrate and butyl aniline, which were probably formed as follows:—



With secondary amines, on the other hand, the main reaction seemed to be one of oxidation. Diphenylamine and ethyl nitrate, on prolonged heating, formed a small amount of the nitrosamine and a much larger amount of a green amorphous solid.

The reaction between a tertiary amine, dimethylaniline, and the nitric esters appeared to be again that of oxidation and condensation of the amine, the product being a violet, viscous dye, which, however, evolved nitrous fumes when it was treated with sulphuric acid.

In the latter experiments the rate at which the violet coloration developed varied considerably with the nature of the nitric ester, being slowest with amyl nitrate and quickest with mannitol hexanitrate. Under similar conditions the intensities of the violet colorations produced in forty hours by the action on dimethylaniline of the following nitric esters were:—

Ethyl nitrate	...	...	...	1
Butyl nitrate	...	...	...	2·85
Amyl nitrate	...	...	...	0·17
Nitrocotton	...	...	...	9·4
Mannitol hexanitrate	...	...	...	22·9

It is likely that these figures represent at least approximately the relative rates of the decomposition of the nitric esters in the presence of dimethylaniline.

This problem is being further investigated.

Experimental.

A. *PRIMARY AMINES.*

(I.) *Aniline.*

(a) *Ethyl Nitrate.*—A mixture of 20 g. aniline and 10 g. ethyl nitrate was heated to 70° C. for several days in a round flask under a reflux condenser. The crystalline solid which separated on cooling the mixture was filtered, washed with petroleum ether, and then extracted with ether in a Soxhlet apparatus. The residue consisted of nearly colourless prisms, which melted with decomposition at 198° C. It was insoluble in ether, scarcely soluble in

alcohol, but dissolved readily in water, affording a solution with a strongly acid reaction. On addition of excess of alkali to the aqueous solution a nearly colourless oil separated. The oil, which boiled at 180–182° C. and gave a purple coloration with bleaching powder, proved to be aniline. The original crystalline solid gave also the characteristic reactions of a nitrate. Its acidity was determined by addition of standard alkali to a weighed amount of the nitrate and titrating the excess of alkali.

On analysis:—

1·3155 g. of substance contained 0·5355 g. HNO_3,
corresponding to HNO_3 40·7 per cent.
$C_6H_5 . NH_2 . HNO_3$ requires HNO_3 40·4 per cent.

The absence of ethyl alcohol from the mother liquor was proved.

At the ordinary temperature of the laboratory a mixture of aniline and ethyl nitrate in the above proportions reacted in the same way, but more slowly, with formation of aniline nitrate.

(b) *Butyl Nitrate.*—An experiment similar to that described above was carried out with aniline and butyl nitrate. The temperature was, however, raised to 100° C., and the heating was continued for only one day. The crystalline solid which formed was filtered and washed with ether, and a further quantity was obtained by addition of ether washings to the filtrate. After purification by ether it melted with decomposition at 198° C., and was found to be identical with the aniline nitrate formed by the interaction of aniline and ethyl nitrate. On analysis it was found that:—

1·7512 g. substance contained 0·7075 g. HNO_3,
corresponding to HNO_3 40·4 per cent.
$C_6H_5 . NH_2 . HNO_3$ requires HNO_3 40·4 per cent.

The mother liquor was mixed with warm water, and the oil which separated was removed, dried, and distilled. The first fraction, which boiled below 200° C. and consisted largely of aniline, was rejected. The second fraction, which boiled between 200° C. and 230° C., consisted of a mixture of aniline and butyl-aniline, while the third fraction, which boiled at 230–240° C., consisted mainly of butyl-aniline. From the last fraction by re-distillation pure butyl-aniline, boiling at 236–238° C., was obtained. Its acid solution formed a nitrosamine with sodium nitrite.

(c) *Amyl Nitrate.*—In another experiment a mixture of 7 g. of aniline and 8 g. of amyl nitrate was heated to 100° C. for eight hours under an air condenser. Excess of ether was added to the contents of the flask when cold. The precipitate was filtered, washed with ether, and dried. It consisted of nearly colourless prisms of aniline nitrate, which was identified by the method described above under ethyl nitrate.

(d) *Mannitol Hexa-Nitrate.*—A mixture of 10 g. aniline and 4 g. mannitol hexa-nitrate was gradually heated from 15° C. to 80°–90° C., when a violent reaction took place, leaving only charred matter in the flask.

(II.) *p-Toluidine.*

(a) *Ethyl Nitrate.*—A mixture of 25 g. *p*-toluidine and 10 g. ethyl nitrate was heated to 100° C. for 4 to 5 hours in a round flask under a reflux condenser. The crystalline solid which was obtained on adding excess of ether to the cooled liquid was filtered, washed with ether, and then extracted with the latter solvent in a Soxhlet apparatus. The residue consisted of colourless rectangular prisms, which melted with decomposition at 202° C. It was insoluble in ether, scarcely soluble in alcohol, but dissolved readily in water, giving a solution with a strongly acid reaction. On addition of alkali an oil separated, which solidified on standing. This solid, which after recrystallization from ether melted at 45° C. and boiled at 199° C., proved to be *p*-toluidine. The original crystals gave also the reactions characteristic of a nitrate. The acidity was determined, as in the case of aniline nitrate, by addition of standard alkali to a weighed quantity of the nitrate and titrating the excess of alkali.

On analysis :—

3·6636 g. of nitrate contained		1·3650 g. HNO_3,
which corresponds to	HNO_3	37·3 per cent.
$CH_3 . C_6H_4 . NH_2 . HNO_3$ requires	HNO_3	37·06 per cent.

The mother liquor after removal of *p*-toluidine nitrate was distilled. Ether came over first, then, as the temperature rose, some unchanged ethyl nitrate distilled. The second fraction, which boiled between 150° C. and 205° C., consisted largely of *p*-toluidine and was neglected. The third fraction, which boiled between 205° C.–220° C., consisted mainly of ethyl-*p*-toluidine. On redistillation, this fraction yielded a small quantity of the pure base, boiling at 215° C.–218° C., the acid solution of which formed a nitrosamine on addition of sodium nitrite.

(b) *Butyl Nitrate.*—A mixture of 30 g. of *p*-toluidine and 18 g. of butyl nitrate was heated to 100° C. for 8 hours in a round flask under a reflux condenser. On cooling, a crystalline solid separated. Excess of ether was added to the liquid, and more solid was obtained. The solid was filtered and washed with ether. The filtrate was returned to the flask, and, after removal of the ether, the heating was continued. At the end of each day the crystalline deposits were removed as described. When no more solid appeared, even on addition of ether (about 7 or 8 days), the heating was discontinued.

The crystalline deposit was extracted with ether in a Soxhlet apparatus for a few hours. The residue consisted of rectangular prisms, which melted with decomposition at 202° C., and were found to be identical with those obtained from ethyl nitrate and *p*-toluidine.

On analysis it was found that :—

1·9526 g. of the substance contained		0·7241 g. HNO_3,
corresponding to	HNO_3	37·1 per cent.
$CH_3 . C_6H_4 . NH_2 . HNO_3$ requires		37·06 per cent.

When concentrated sulphuric acid was poured gently down the side of a test tube containing an aqueous solution of *p*-toluidine nitrate, a red violet ring formed at the junction of the two layers. The colour changed rapidly to dark brown.

The mother liquor was distilled. The first fraction, boiling below 100° C., consisted almost entirely of ether. The second fraction, which was collected up to 150° C. under 80 mm., was found to be a mixture of unchanged butyl nitrate with *p*-toluidine. The third fraction, boiling between 150° C. and 180° C. at 80 mm., consisted of *p*-toluidine and butyl-*p*-toluidine. The fourth fraction boiled between 180° C. and 200° C. at 80 mm., and consisted chiefly of butyl-*p*-toluidine. From this last fraction, by redistillation in vacuo, pure butyl-*p*-toluidine was obtained. It boiled at 250° C.–251° C. under 750 mm. Its acid solution gave a nitrosamine with sodium nitrite.

(c) *Amyl Nitrate.*—A mixture of 4 g. *p*-toluidine and 2 g. amyl nitrate was heated at 100° C. for 4 hours. On adding excess of ether to the cold solution, colourless rectangular prisms, which melted with decomposition at 202° C., separated. The substance was identified as *p*-toluidine nitrate by the method described under ethyl nitrate and butyl nitrate.

(III.) *Ortho-Toluidine.*

(a) *Ethyl Nitrate.*—A mixture of 40 g. *o*-toluidine and 10 g. ethyl nitrate was heated to 100° C. for 5 hours in a round flask under a reflux condenser. Excess ether was added to the cold solution, and the crystalline solid which separated was filtered, washed with ether, and finally freed from soluble matter by means of ether in a Soxhlet apparatus. The residue was found to consist of badly formed crystals, melting with decomposition at 189° C. It was insoluble in ether, scarcely soluble in alcohol, but was readily soluble in warm water, yielding a solution of pronounced acid reaction. It proved to be the nitrate of *o*-toluidine. With concentrated sulphuric acid, an aqueous solution of the nitrate gave a brown ring at first, whereas with *p*-toluidine nitrate a violet ring formed first.

On analysis:—

0·9628 g. substance was found to contain 0·3565 g. HNO_3,
corresponding to HNO_3 = 37·03 per cent.
$CH_3 . C_6H_4 . NH_2 . HNO_3$ requires HNO_3 = 37·06 per cent.

(b) *Butyl and Amyl Nitrates.*—In separate experiments it was found, as would be expected from the above work, that *o*-toluidine reacted with both butyl nitrate and amyl nitrate, forming *o*-toluidine nitrate.

(IV.) *m-Xylidine.*

m-Xylidine nitrate was formed by heating mixtures of the base with ethyl nitrate, butyl nitrate, and amyl nitrate, respectively, to 100° C.

It consisted of colourless prisms, which melted with decomposition at 208–209° C. It was scarcely soluble in alcohol, insoluble in ether, and dissolved readily in warm water. *m*-Xylidine, boiling at 210° C., was separated from it by addition of excess of alkali.

On analysis it was found that:—

1·1040 g. substance contained		0·3781 g. HNO_3,
corresponding to	HNO_3	34·25 per cent.
$(CH_3)_2 . C_6H_3 . NH_2 . HNO_3$ requires	HNO_3	34·24 per cent.

B. *SECONDARY AMINES.*

(I.) *Monomethylaniline.*

(a) *Butyl Nitrate.*—A mixture of 5 g. monomethylaniline with an equal weight of butyl nitrate was heated at 100° C. for several days under a reflux condenser. After about 8 hours a reddish-violet coloration appeared, which became deeper on continued heating. After four days the heating was discontinued, and the violet-coloured viscous solid was extracted with petroleum ether and then with chloroform. On evaporation of the chloroform a reddish-violet viscous mass remained. The substance was insoluble in ether, but soluble in chloroform, alcohol, and in acids, giving brown solutions. On addition of alkali, a light green precipitate formed.

(b) *Mannitol Hexanitrate.*—An experiment similar to that described above was performed using 5 g. of monomethylaniline and 2 g. of mannitol hexanitrate in 20 c.c. of alcohol. After heating for a few hours, a deep reddish coloration formed. After two days the alcohol solution was evaporated, and the residue extracted with petroleum ether and cold chloroform, in which mannitol hexanitrate is not very soluble. A viscous reddish-violet tar resulted, similar to that obtained by interaction of butyl nitrate with monomethyaniline, and resisted all attempts at crystallization. It was soluble in chloroform, alcohol, and acetone, insoluble in water, but soluble in acids, giving a deep brown solution from which a light green precipitate was formed on addition of alkali.

(II.) *Diphenylamine.*

(a) *Ethyl Nitrate.*—(1) A mixture of 2 g. diphenylamine and 6 g. ethyl nitrate was heated on a water bath for a day. The solution, which at first was only very slightly brown in colour, became much darker, and finally black. The excess of ethyl nitrate was then distilled off, and the residue was dissolved in a small quantity of alcohol, from which an oily solid was obtained on addition of water. On filtering, a light-coloured solid, melting at 53° C., was obtained. It consisted of a mixture of diphenylnitrosamine with diphenylamine.

(2) A similar experiment was carried out using 6 g. diphenylamine and 20 g. ethyl nitrate, the time of heating being extended to 24 hours. The excess of ethyl nitrate was distilled off and the tarry residue was distilled in steam;

two fractions were collected; the first consisted of nearly pure diphenylamine, the second containing a mixture of diphenylnitrosamine with diphenylamine. The substance (m.p. 52° C.) was fractionally crystallized from alcohol, but no pure diphenylnitrosamine could be obtained, as the amount present was too small.

(3) In another experiment 12 g. of diphenylamine and 40 g. ethyl nitrate were heated on a water bath for 300 hours in a round flask under a reflux condenser. After removal of excess ethyl nitrate a black tarry residue was obtained. This was dissolved in benzene, and petroleum ether was added. The precipitate which separated was filtered off and freed from soluble matter by extraction with anhydrous ether for 8 hours in a Soxhlet apparatus. The residue consisted of a dark green amorphous powder, which melted with decomposition at 278° C. The substance was soluble in alcohol, chloroform, acetone, acetic acid, and benzene (but did not crystallize), insoluble in water, petroleum ether, or anhydrous ether.

On analysis :—

0·0818 g. of the substance gave 7·2 c.c. nitrogen at 11·5° C./739 mm.,

and 0·1395 g. of the substance gave 0·3820 g. CO_2 and 0·0634 g. H_2O corresponding to :—

C = 75·76, H = 5·1, N = 10·32, O = 8·82, per cent.

The filtrate after removal of the green solid was evaporated and a tarry mass remained. This was extracted several times with hot ligroin. The extract on standing deposited oily crystals, which were filtered off and distilled in steam; the distillate was filtered from a yellowish solid which melted at 49° C. and consisted of a mixture of diphenylamine and diphenynitrosamine. The amount of diphenylamine present in the mixture was estimated by adding a known volume of decinormal alcoholic iodine to a known weight of the substance dissolved in an alcoholic solution of mercuric chloride (40 g. per litre), and allowing the mixture to stand for 15 minutes in the dark; the excess of iodine was titrated with standard sodium thiosulphate. Under the above conditions diphenylamine forms a di-iodo derivative, while diphenylnitrosamine is unacted upon.

On analysis of the solid :—

0·0800 g. absorbed 16·6 c.c. N/10 Iodine,
corresponding to 87·5 per. cent of diphenylamine.

(b) *Butyl Nitrate.*—A mixture of 25 g. diphenylamine and 10 g. butyl nitrate was heated to 100° C. for 200 hours in a round flask with a reflux condenser. Excess butyl nitrate was removed by distillation in vacuo, and a tarry solid remained. The solid was extracted with warm ligroin, and the extract, on standing, deposited an oily semi-crystalline mass, which was distilled in steam. The solid residue in the distillate was dried and recrystallized from

alcohol. Yellowish plates were obtained melting at 48° C. and giving a blue coloration with sulphuric acid.

On analysis :—

0·894 g. of the substance absorbed 14·15 c.c. N/10 Iodine, which corresponds to 0·0598 g. diphenylamine = 65·7 per cent.

C. *TERTIARY AMINE.*

Dimethylaniline.

(a) *Ethyl Nitrate.*—A mixture of 2·2 g. dimethylaniline and 10 g. ethyl nitrate was heated to 100° C. for several days in a flask under a reflux condenser. After about 20 hours heating a reddish-violet coloration appeared, which became deeper on continued heating. After heating for 10 days, excess of ethyl nitrate was removed, and a dark violet tarry solid, scarcely soluble in ether or water, was obtained. The substance was soluble in mineral acids, forming green solutions (or brown solutions with excess of acid), from which the original reddish-violet compound was reformed on addition of alkali.

It dyed silk and wool directly. The former fabric assumed a rich purple colour, and the latter a navy blue. With concentrated sulphuric acid the solid evolved oxides of nitrogen.

(b) *Butyl Nitrate.*—A mixture of 10 g. dimethylaniline and 2·5 g. butyl nitrate was heated in a flask under a reflux condenser, on a boiling water-bath for several days. The liquid gradually assumed a reddish-violet colour, which increased in intensity on continued heating. After several days the liquid was distilled, and a reddish-violet tarry residue was obtained, which was shown to be identical with that formed by the interaction of ethyl nitrate with dimethylaniline.

(c) *Amyl Nitrate.* — An experiment, similar to that already described, was carried out using 10 g. amyl nitrate and 2·5 g. dimethylaniline. In this case also a reddish-violet residue was obtained, which had all the properties of the substance got in the other reactions of dimethylaniline with nitric esters.

(d) *Glyceryl Trinitrate.*—In this experiment about 0·5 g. of glyceryl trinitrate was dissolved in 20 c.c. of acetone, and 5 g. of dimethylaniline were added. The mixture, contained in a flask fitted with a reflux condenser, was heated at 60° C. on a water bath for several days. A reddish-violet coloration, gradually increasing in intensity, appeared after about 2 hours. The colour was exactly the same as that obtained in the reactions of dimethylaniline and other nitric esters. No attempt was made to obtain the residue in this case.

(e) *Nitrocellulose.*—A mixture of 2 g. of nitrocotton with 50 c.c. of acetone and 2 c.c. of dimethylaniline was heated at 60° C. In about 2 hours a deep reddish-violet colour appeared, and increased in intensity with continued heating as before.

When a few c.c. of the solution were acidified with hydrochloric acid a green solution was formed. On adding alkali the violet colour was restored.

(f) *Mannitol Hexanitrate.*—(1) A mixture of 20 g. dimethylaniline and 20 g. mannitol hexanitrate was heated from 15° C. When near 100° C. a violent reaction took place, much nitrous fumes were evolved and a reddish-violet residue, which was proved to be identical with that already obtained, remained in the flask.

(2) A mixture of 20 g. dimethylaniline and 20 g. of mannitol hexanitrate, to which 40 c.c. of chloroform had been added, was heated gradually up to 70° C. The liquid darkened in colour, and in about 15 minutes a deep reddish-violet coloration had formed. Brown fumes were evolved. After 6 hours the liquid was cooled and filtered; the filtrate was evaporated, and, when all the chloroform had disappeared, the reddish-violet residue was extracted with ligroin and petroleum ether prior to its examination.

(3) A mixture of 5 g. mannitol hexanitrate, 2 g. dimethylaniline, and 25 c.c. chloroform, was heated to 70° C. for two days, and the gases evolved were collected, over dilute caustic soda solution. 500 c.c. of gas were collected, which on analysis contained 30 per cent. nitrogen and 70 per cent. nitric oxide.

Relative Speeds of the Decomposition of certain Nitric Esters in the Presence of Dimethylaniline.

Since the colouring matter produced by the action of alkyl nitrates on dimethylaniline appeared to be independent of the nature of the alkyl radical, it occurred to us that perhaps the formation of this colouring matter might be utilised to give a rough comparison of the speeds of the decomposition of the esters by the base.

In the first series of experiments 2 c.c. of dimethylaniline were dissolved in 25 c.c. of chloroform, and 3 molecular amounts of the ester (ethyl nitrate, butyl nitrate, or amyl nitrate) were added in each case. The flasks were then heated under reflux condensers at 70° C. for several days (8 hours each day). At intervals, one cubic centimetre of the solution was withdrawn from each of the flasks and diluted to 10 c.c. with alcohol. The intensities of the colorations were then compared with that of a solution of the coloured body in alcohol, which served as a standard of comparison, and a graph of intensity of coloration (expressed as a multiple of the standard) and time was plotted.

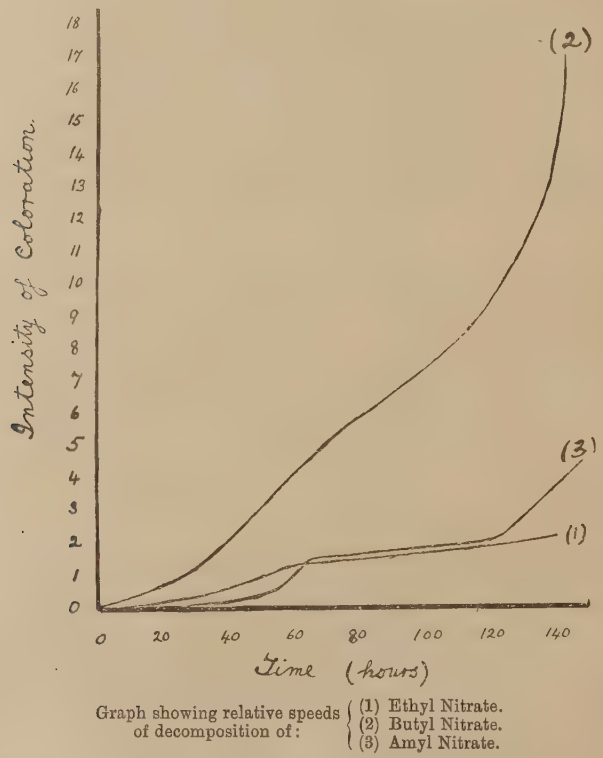
The results are given in Fig. 1.

In the second series of experiments mixtures of 2 g. of the nitric ester (nitrocotton or mannitol hexanitrate) with 2 c.c. of dimethylaniline and 50 c.c. of acetone were heated to 60° C. for several days. The intensities of the colorations produced were expressed as multiples of the same standard as before, and the graphs were plotted as in the previous experiments.

The results are given in Fig. 2.

Summary.

1. The course of the reactions between primary aromatic amines and nitric esters seems to be indirectly hydrolytic. Thus aniline *o*- and *p*-toluidine, and *m*-xylidine reacted with ethyl, butyl, and amyl nitrates to form the nitrate of the base. In those cases which were fully investigated the alkyl derivative of the base was also formed.



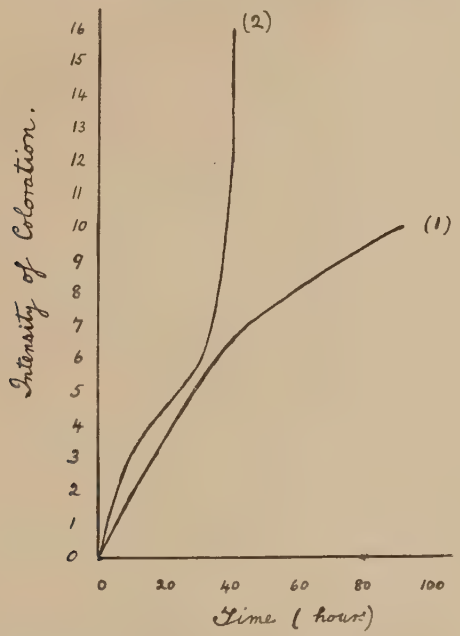
Graph showing relative speeds of decomposition of: (1) Ethyl Nitrate. (2) Butyl Nitrate. (3) Amyl Nitrate.

Fig. 1.

2. The chief reaction between a secondary amine and a nitric ester seems to be one of oxidation, a slight degree of nitration also occurring. Thus monomethyl aniline and butyl nitrate formed a red viscous product, while diphenylamine and ethyl nitrate gave a green amorphous solid. Diphenylnitrosamine was also formed.

3. Tertiary amines are also oxidised by nitric esters. Dimethylaniline was converted into a violet viscous solid, with evolution of oxides of nitrogen.

The reactions between dimethylaniline and the nitric esters of polyhydric alcohols are much more rapid than those between the base and the monohydric alcohols. If the relative speeds of decomposition of nitric esters be measured by the colorations produced with dimethylaniline, the speeds of decomposition



Graph showing relative speeds of decomposition of: (1) Cellulose Nitrate. (2) Mannitol Hexa-Nitrate.

Fig. 2.

of ethyl, butyl, amyl, cellulose, and mannitol nitrates, when heated for 40 hours with dimethylaniline, are in the ratio 1, 2·85, 0·175, 9·4, and 22·9 respectively.

In conclusion we wish to state that this research was undertaken at the request of the Research Section of Nobel's Explosives Company, to whom we desire to express our thanks for a grant in aid of the investigation.

No. 12.

THE COMMERCIAL UTILISATION OF JAVA CITRONELLA OIL.

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The object of this investigation was to determine whether it would be possible to prepare high-class perfumes from the crude Java Citronella Oil, which this country imports for use in household soaps. The crude oil is obtained from *Cymbopogon nardus* grass of the *Maha pangiri* type, which grows in Java and Ceylon, by distillation with steam. In the perfume industries, it is used chiefly for the cheaper varieties of soap, but on account of its marked, and somewhat harsh, odour it is not suitable for scenting high-grade toilet soaps. The crude oil contains, nevertheless, some valuable odoriferous bodies, that of Java being in this respect the richer. It is possible to separate these high-grade perfumes, and also to convert them into other valuable derivatives.

Java Citronella Oil appears in the market in different qualities, due either to variation in the contents of the more valuable odoriferous bodies or to deliberate adulteration of the oil. In selecting an oil suitable for our investigation it was necessary, therefore, to apply some simple physical and chemical tests to various commercial samples, and to compare the results got from them with those from a standard specimen. The chemical analysis, more especially, besides affording criteria of the genuineness of a sample, also gives indications of the method to be adopted in the separation of the high-grade constituents from the crude oil.

Amongst the constituents of Java Citronella Oil are Citronellal, Geraniol, Citronellol, small amounts of esters of these alcohols, and some terpenes. Of these, the alcohols and the aldehyde are the valuable constituents—the latter being the parent substance of citronellol and hydroxy-citronellal, which form the basis of Lily and lilac perfumes, and the others the essential ingredients of all synthetic Rose perfumes. Since these substances are liquids, and boil at nearly the same temperatures, their separation by fractional distillation was not possible. An attempt was, therefore, made to separate them by chemical methods, depending on differences in their constitution and properties.

Citronellal, an aldehyde, combined with sodium bisulphite to form a solid substance, consisting mainly of a normal mono-bisulphite with a small amount of another solid, produced by the inter-action of one molecular amount of the aldehyde with two molecular amounts of the bisulphite. From the normal bisulphite the aldehyde was readily liberated by treatment with dilute alkali. The aldehyde was further purified by distilling—first in steam, afterwards under reduced pressure. The product contained, however, some isopulegol, formed from the citronellal during the progress of the separation. (F. Tiemann. Ber., **32** (1899), p. 8257; Cf. Labbé Bull. Soc. Chim. III, **21** (1899), p. 1023.)

The oil from which the citronellal had been separated was then hydrolysed by warming it with alcoholic potash, and the geraniol contained in it was separated from citronellol by taking advantage of the fact that geraniol forms a crystalline double compound with calcium chloride, whereas no such crystalline body is formed by citronellol. From the double compound of geraniol and calcium chloride the alcohol was separated by decomposition with water, followed by distillation in a current of steam.

The residual oil still contained some geraniol, citronellol, and terpenes. An attempt was made to separate citronellol from this mixture by means of phthalic anhydride, but, as this proved unsuccessful, the attempt to separate citronellol was not further pursued.

Attention was then given to the citronellal, which formed from 35 to 45 % of the crude oil. The aldehyde itself is not very valuable, since it possesses a somewhat harsh odour, and is unstable towards air, alkalies, and acids. Reduction to the corresponding alcohol would, however, convert it into the very valuable perfume, citronellol. This we attempted to effect by means of several reducing agents—including iron and acetic acid, sodium amalgam and acetic acid, and aluminium amalgam and water. Both the amalgam methods gave satisfactory results, although neither of them seemed capable of being converted into an economically commercial process under Irish conditions. Preliminary experiments were then made on the electrolytic reduction of citronellal, and it was found that with lead electrodes and dilute alkali as the electrolyte, a yield of citronellol up to about 80 % could be readily obtained.

Experimental.

I.—*EXAMINATION OF CRUDE JAVA CITRONELLA OIL.*

The crude Java Citronella Oil employed by us in the experiments described below had a specific gravity of 0·8918 at 15° C., and in a one-decimetre tube had an angle of optical rotation $(-\alpha_D) = -2°48$. Genuine standard Java Citronella Oil has a specific gravity between the limits of 0·881 and 0·900, and an angle of optical rotation between $-1°$ and $-3°$.

To determine its acetylisable contents and esters.—About 20 c.c. of the oil were heated to gentle boiling for two hours with 40 c.c. of acetic anhydride

and 4 g. of anhydrous sodium acetate. The excess of acetic anhydride was then converted into acetic acid by warming the mixture with water for a quarter of an hour. After cooling, the oil was separated, washed with a salt solution, and dried over anhydrous sodium sulphate. In this way geraniol and citronellol were converted into their acetates, and citronellal into isopulegyl acetate. Of the dried oil, 2 g. were heated in a flask with 10 c.c. of alcohol and 20 c.c. of semi-normal potash for two hours. The excess of alkali was titrated by means of semi-normal acid, and the percentage of acetylisable contents and esters was calculated by means of the formula— $P = \frac{am}{20(s - 0{\cdot}021\,a)}$, in which P is the percentage of acetylisable contents and esters; m is the molecular weight of the acetate, $C_{10}H_{17}OOCCH_3$; a is the number of c.c. of N/2 KOH used; s is the number of grammes of acetylated oil taken. In this sample the percentage of acetylisable contents and esters found was 83·3.

The percentage of aldehyde in the oil was determined by means of sodium bisulphite. A mixture of 10 c.c. of the oil, with an equal volume of 30 % sodium bisulphite solution (free from excess of sulphur dioxide), was well shaken in an "aldehyde flask." The flask was heated in the water-bath, and more bisulphite was added from time to time, with frequent shaking and heating, for some hours, until the flask was half filled. The flask was then cooled, and bisulphite solution was added, until the whole of the uncombined oil was in the graduated neck of the flask. The volume of the oil was then read, and that of the aldehyde was then found by difference. The percentage of aldehyde (citronellal) contained in the oil was 45.

II.—*SEPARATION OF CITRONELLAL AND GERANIOL FROM CITRONELLA OIL.*

1. *Citronellal.*

About 500 c.c. of Java Citronella Oil was placed in a wide-mouthed vessel, and cooled to 0° C. An equal volume of 30 % sodium bisulphite solution (free from excess of SO_2) was cooled to 0° C. and added to the citronella oil.

The contents of the vessel were stirred vigorously, and kept cool by means of a freezing mixture of ice and salt. After addition of excess of sodium bisulphite, and further stirring, the mixture was set aside for four hours. Citronellal bisulphite, containing 1–2 % of the double bisulphite, separated in the solid state.

This was filtered, and freed from traces of oil by washing with ether. It was then added to a litre of water containing from 10–15 g. of potash. The citronellal which separated from the aqueous solution was distilled in a current of steam, and purified still further by distillation under reduced pressure.

The yield was 240 c.c. It had the physical constants set out below. For

the purpose of comparison, the average physical constants obtained by various workers are given in the last column.

B.P.	205–206° C. (with slight decomposition)	205–208° C. (with slight decomposition)
Density	0·8845 at 19·5° C.	0·8570 at 15° C.
α_D (optical rotation),	2° 24′	10° 5′
n_D	1·472 at 18·3° C.	1·4465 at 20° C.

The somewhat high density and low "angle of optical rotation" indicates that the citronellal thus got probably contained some isopulegol.

When this method for extracting citronellal was applied on a larger scale, the following results were obtained:—

Weight of Citronella Oil.	Yield of Citronellal.
lbs.	lbs.
3	1·5
9½	4
15	6
23	10

The average yield of citronella was, thus, about 43% of the weight of the crude oil.

2. *Geraniol.*

The oil which remained after the extraction of the citronellal from crude Java Citronella Oil was heated to boiling for an hour with dilute alcoholic potash. The oil was separated, washed with water, and dried over anhydrous sodium sulphate. An equal weight of finely-powdered, anhydrous calcium chloride was added to it in an air-tight vessel. After intimate mixing, the product was set aside for eight hours. By the end of this period the mixture had set to a semi-solid mass, with some oil floating on top. The oil was separated, the solid mass was broken up, and then washed with ligroin, contact with moist air being prevented as far as possible. The solid geraniol calcium chloride was decomposed by water, and the geraniol set free was distilled in a current of steam. From 200 c.c. of the oil 70 c.c. of geraniol were obtained. It was further purified by distillation under reduced pressure. On examination, the following results were obtained, and, for purposes of comparison, the average results got by various workers are included in the last column:—

B.P. at 12 mm.	114–115° C. ...	114–115° C.
Density ...	0·8811 (at 19·5° C.)	0·885 (at 15° C.)
α_D ...	± 0	± 0
n_D ...	1·4768 (at 18·3° C.)	1·4770 (at 20° C.)

By the above process only about 70 % of the theoretically possible amount of geraniol could be extracted. The separation of the uncombined oil from the solid geraniol calcium chloride by means of ether was not practicable, since ether dissolves the solid molecular compound to an appreciable extent. With petroleum ether, and ligroin this loss does not occur, but the former solvent appears to decrease the odoriferous value of the perfume finally obtained.

After removal of the citronellal and the major portion of the geraniol, the oil still contained citronellol, terpenes, and some geraniol. A few attempts were made to isolate the citronellol from this mixture as its phthalate. These were not successful, and the attempts were not continued. The residual oil had a strong, harsh, terpene odour, and could be used only in common household soaps.

III.—*REDUCTION OF CITRONELLAL.*

1. *By means of Iron and Acetic Acid.*

(*a*) In this experiment 37 g. of citronellal were added to a flask containing 160 g. of iron filings and 300 c.c. of a 50 % acetic acid solution. The reaction was allowed to proceed at the ordinary temperature for twelve hours, and the mixture was then heated for eight hours under a reflux condenser. On cooling, the mixture set to a dark, solid mass. The mixture was heated to boiling, and separated from the undissolved solid, which was washed with ether. The oil got from the separated liquid and that left by evaporation of the ether were mixed, hydrolysed, and distilled in a current of steam. The yield was poor, and consisted of citronellol containing some isopulegol.

(*b*) In the second experiment the amounts of iron filings and acetic acid were reduced to half the above quantities, and when the reaction was finished the resulting oil was distilled directly in a current of steam. Although the product finally got contained less isopulegol than in the previous experiment, the use of iron and acetic acid for the conversion of citronellal into citronellol did not seem likely to become the basis of a commercial process.

2. *By means of Sodium Amalgam and Acetic Acid.*

(*a*) A solution of 50 g. of citronellal in about 600 c.c. of alcohol was placed in a large round flask contained in a freezing mixture of ice and salt. An amalgam of 50 g. of sodium with 950 g. of mercury was finely powdered, and added in small quantities to the alcoholic solution. After each addition of the sodium amalgam about 10 c.c. of glacial acetic acid were added, until the total amount of acetic acid added was 150 c.c. The whole process lasted about eight hours, and was conducted in such a manner that the solution was never allowed to become more than faintly acid, nor the temperature to rise above 5° C. After remaining overnight, about 50–60 g. of potassium hydroxide were added, and the mixture was heated for a few hours, so as to destroy any unchanged citronellal. The solution was then separated from the mercury; the alcohol was removed by heating on a water-bath, and the residual oil was distilled in

a current of steam. The citronellol thus got had a pale yellow colour, and contained some isopulegol.

(*b*) In another experiment the mixture, after addition of the sodium amalgam and acetic acid, was allowed to remain two days before being further treated as in the last experiment. Yields of citronellol (containing some isopulegol) amounting to about 73% were obtained.

(*c*) By reducing the amount of alcohol from 600 c.c. to 200 c.c., but otherwise proceeding as in experiment (*b*), it was found that 50 c.c. of citronellal gave 37 c.c. of citronellol, which was, however, still slightly impure.

(*d*) These experiments were performed using 100 g. of citronellal, 400–450 c.c. of alcohol, 300 c.c. of acetic acid, and 2,000 g. of 5 % sodium amalgam. The method was similar to that just described, but the time of adding the sodium amalgam was extended over two days, one-half of the sodium amalgam and acetic acid being added each day. The yields of citronellol were 75 c.c., 76 c.c., and 77 c.c. respectively.

(*e*) A final experiment was made with 300 c.c. of citronellal, 1,200 c.c. of alcohol, 6,000 g. of sodium amalgam, and 900 c.c. of acetic acid. The citronellal in this case was purified before use by distillation in a current of steam. The addition of the amalgam extended over three days. The yield of citronellol was 220–225 c.c.

A sample of this citronellol distilled under reduced pressure gave the following results, and, for the purpose of comparison, the constants given by a foreign firm of international reputation are shown in the last column:—

B.P.	110–112° at 10 mm.	109° at 7 mm.
Density ...	0·8542 at 19·5°C.	0·8604 at 15° C.
α_D	2° 49′	2° 20′
n_D	1·468 at 18·3°C.	1·4572 at 15° C.

3. *By means of Aluminium Amalgam.*

Thin rectangular strips of aluminium foil were immersed for a short time in a dilute solution of sodium hydroxide, and then well washed with water. These strips were next placed for a few minutes in a solution of mercuric chloride, and after washing with water the strips thus amalgamated were ready for use.

Several preliminary experiments were made with a view to determining the best temperature and the most suitable relative proportions of the aluminium amalgam and the citronellal for the reaction. As a result of these, it was found that the reaction proceeds best at 60–70° C., and is most economically carried out when the amount of aluminium amalgam added for the reduction of a given weight of citronellal is about four times that required theoretically.

In one of these experiments 100 c.c. of citronellal, 400 c.c. of alcohol, and 20 c.c. of water were placed in a large flask, and the amalgam prepared from

22 g. of aluminium was added. The temperature was allowed to rise to 60–70° C., and was maintained between these limits until the reaction was complete. The citronellol was then distilled in a current of steam. The yield obtained was 74 c.c.

Some experiments were then performed, using 500, 1,000, 2,000, and 3,000 c.c. of citronellal, with the corresponding amounts of aluminium amalgam and alcohol. The reaction vessel was, in each case, cooled by water, so that the temperature remained at 60–70° C. during the experiment. The aluminium amalgam was removed, and re-activated when necessary. In each case, when all the aldehyde had been reduced, the citronellol was separated by distillation in a current of steam. The yield varied between 70 and 75 % of the citronellal.

In all these experiments the bubbles of gas formed on the aluminium amalgam tended to make the latter rise to the surface of the solution. This was not desirable, since the amalgam on contact with air oxidised very readily with evolution of much heat. This difficulty was overcome by enclosing the amalgamated strips in a cage made from strong iron netting of fairly fine mesh.

4. *By means of Electrolytic Reduction.*

Several experiments were made in order to determine the best conditions for the electrolytic reduction of citronellal to citronellol. The experiments were carried out in a divided cell, the outer compartment being separated from the inner anodic compartment by a porous pot.

In one experiment we put 30 c.c. of citronellal and 90 g. of sodium sulphate in the outer cathodic compartment, and a concentrated aqueous solution of sodium sulphate in the inner compartment. A current of 2 amperes was passed for eight hours from the carbon anode to a mercury cathode. At the end of this time the oil formed was separated. It measured about 20 c.c., and consisted mainly of isopulegol.

By doubling the current strength and decreasing the time to one-half a product was got which contained a much smaller amount of isopulegol.

In another experiment it was found that by increasing the cathode surface, by substituting thin plates of lead for the mercury, a better result was obtained, due, no doubt, to the greater over-voltage of the lead as well as to the lower current density. In all these experiments, however, the acid formed in the anodic compartment diffused into the cathode space, and exercised deleterious action on the citronellal.

An attempt was made to overcome this difficulty by using dilute sodium hydroxide solution as the electrolyte.

About 10 g. of sodium hydroxide, dissolved in the least possible amount of water, were added to 1,000 c.c. of 60% alcohol, and in this 250 c.c. of citronellal were dissolved. This solution was placed in the outer compartment of the cell, and a concentrated solution of sodium hydroxide was put into the inner compartment, and was renewed as required during the course of the experiment. A current of 8–9 amperes was passed through the cell for 10 hours. By cooling

the cell with water the temperature was kept at 50–60° C. during the electrolysis. The yield of citronellol, separated as in the above experiments, was about 80 % of the citronellal. A sample of this, when further purified by distillation under reduced pressure, boiled at 108–110° C. under a pressure of 12·5 mm.

IV.—*ACETATES OF GERANIOL AND CITRONELLOL.*

Little difficulty was experienced in preparing these substances, which have already been made abroad.

From 200 c.c. of geraniol, 32·2 c.c. of acetic anhydride, and 44 g. of powdered anhydrous sodium acetate 220 c.c. of geranyl acetate were prepared by heating to 140–150° C. for an hour under a reflux condenser, and removing the excess of acetic anhydride by warming with water. When this was purified by distillation under reduced pressure it gave the following results, which may be compared with those given by the product of a continental manufacturer in the last column:—

B.P.	127–129° C. at 15 mm.	127·8–129·2 at 16 mm.
Density ...	0·907 at 19·5° C.	0·91–0·917 at 15° C.
n_D	1·4637 at 18·3° C.	1·462–1·466 at 20° C.
α_D	± 0	± 0

Similarly, from 500 c.c. of citronellol, 500 c.c. of acetic anhydride, and 100 g. of powdered anhydrous sodium acetate, about 525 c.c. of crude citronellyl acetate were got by heating for two hours to a temperature of 140–150° C. After removal of the excess of acetic anhydride by means of warm water, the oil was separated from the aqueous solution, and washed free from acid with the aid of a solution of common salt. It was then dried over anhydrous sodium sulphate, and a specimen of it was further purified by distillation under reduced pressure. On examination, it gave the following results, which may be compared with those contained in the last column, for samples of citronellyl acetate made on the Continent:—

B.P. at 15 mm.	119–121° C. ...	119–121° C.
Density ...	0·9035 at 19·5°C.	0·9013 at 15° C.
α_D	+ 0° 30′	+ 2° 37′ to – 10° 15′
n_D	1·457 at 18·5° ...	1·4489 at 20°

The preparation of geranyl-methylether was not examined fully. In the first experiment geraniol was treated with dimethyl sulphate and alcoholic potash. The product consisted mainly of unchanged geraniol, and contained only a small amount of geranyl-methylether. Replacement of the dimethyl sulphate by methyl iodide was not more successful. Finally, a small yield of geranyl-methylether was got by gently heating under a reflux condenser a solution of sodium in dry geraniol with methyl iodide.

No. 13.

THE ACTION OF ALCOHOLIC HYDROCHLORIC ACID ON METHYLDIPHENYLTETRAHYDROPYRONE.

By HUGH RYAN, D.Sc., and J. J. LENNON, Ph.D.

[Read May 22. Published separately November 2, 1928.]

In a previous communication (Proc. Roy. Irish Acad. (1925), **37**, B, p. 27), it was shown that the tri-condensation product of benzaldehyde and methylethylketone obtained by Ryan and Devine (Proc. Roy. Irish Acad. (1916), **32**, B, 208), was identical with benzylidenemethyldiphenylcyclopentenone (VI, see diagram) prepared by direct synthesis. It was further shown that γ-benzylidenemethylethylketone (II) reacted with one molecule of benzaldehyde in the presence of dilute alkali to form *iso*-methyldiphenylcyclopentenone (IV), and that this last substance was converted into benzylidenemethyldiphenylcyclopentenone by the action of benzaldehyde in the presence of alcoholic hydrochloric acid, the course of the reaction being traced by the conversion of *iso*-methyldiphenylcyclopentenone into methyldiphenylcyclopentenone (V) by the action of dilute alcoholic hydrochloric acid. Since Ryan and Devine obtained benzylidenemethyldiphenylcyclopentenone by the action of benzaldehyde on methyldiphenyltetrahydro-γ-pyrone (III) in the presence of alcoholic hydrochloric acid, it appeared that the first stage in this reaction was the conversion of the tetrahydropyrone derivative into the pentenone derivative (V) by the action of the hydrochloric acid, and it was with the object of proving this that the present work was undertaken.

Methyldiphenyltetrahydro-γ-pyrone (III) has been prepared by several workers. Harries and Müller (Ber. (1902), **35**, 968) obtained the pyrone melting at 68·5° by the action of benzaldehyde on α-benzylidenemethylethylketone. Japp and Maitland (Jour. Chem. Soc. (1904), **85**, 1488) obtained two compounds by the action of two molecules of benzaldehyde on one molecule of methylethylketone, melting at 82–83° and 102–103°, respectively. These substances were considered to be stereo-isomeric methyldiphenyltetrahydro-γ-pyrones, and the same compounds were obtained by the action of benzaldehyde on α-benzylidenemethylethylketone. Ryan and Devine (*loc. cit.*) obtained the tetrahydropyrone derivative melting at 81–83°, and, by comparing the oximes of the two compounds, showed the substance to be identical with that obtained by Harries and Müller.

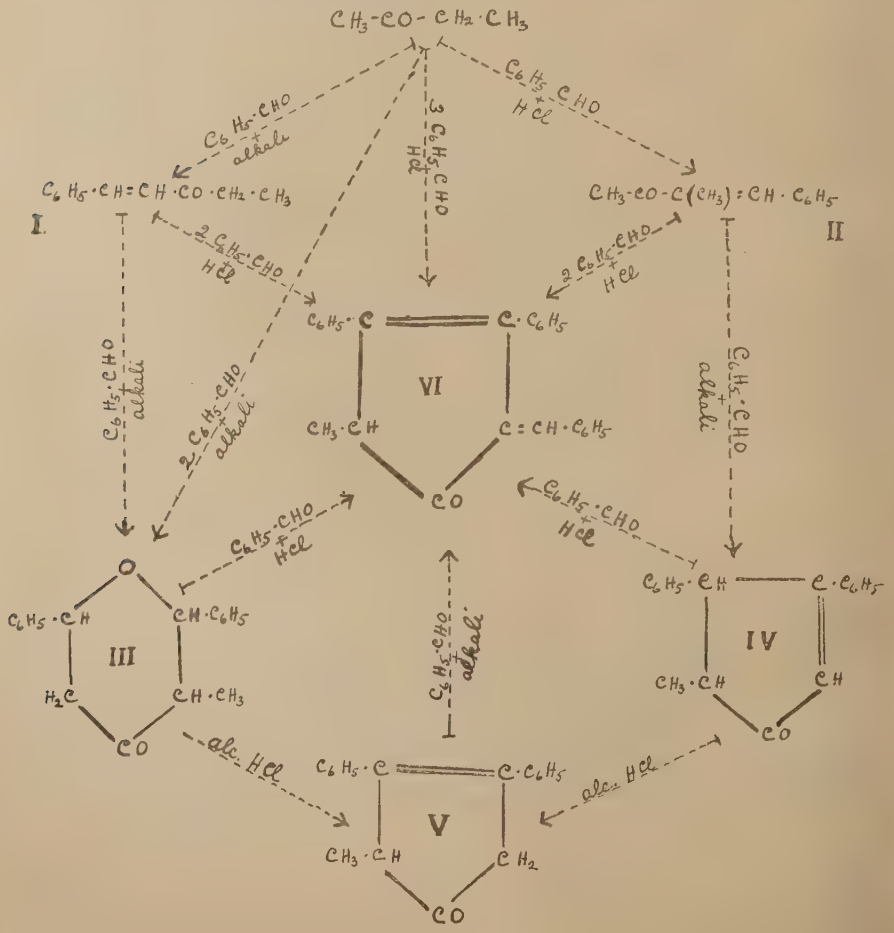
The methyldiphenyltetrahydro-γ-pyrone required for the present work was prepared by a modification of the methods previously described. It was found that when α-benzylidenemethylethylketone and benzaldehyde were allowed to stand in the presence of alcoholic sodium hydroxide the product generally consisted of a gummy mass, from which it was difficult to obtain a crystalline

substance. The required compound was obtained in good yield, however, by allowing the reaction to take place during several weeks, using very dilute aqueous alkali as a condensing agent.

The action of alcoholic hydrochloric acid on methyldiphenyltetrahydro-γ-pyrone was first investigated by Japp and Maitland (*loc. cit.*), but their experiments led to no definite results. While our experiments on the action of dilute alcoholic hydrochloric acid on the tetrahydropyrone derivative were equally unsuccessful, we found that when a large volume of the concentrated acid was employed, under the conditions detailed, the expected methyldiphenylcyclopentenone (V) could be isolated from the reaction product.

We include in this communication an account of the direct conversion of γ-benzylidenemethylethylketone (II) into benzylidenemethyldiphenylcyclopentenone (VI) by the action on it of benzaldehyde in the presence of concentrated alcoholic hydrochloric acid.

The results of the researches on the condensation of benzaldehyde with methylethylketone may now be summarised by the following:—



EXPERIMENTAL.

Preparation of Methyldiphenyltetrahydro-γ-pyrone.

20 g. of γ-benzylidenemethylethylketone, 13·2 c.c. of benzaldehyde, and 1·5 g. of potash in 280 c.c. of water were mixed, and allowed to stand, with occasional shaking, in a stoppered bottle. At the end of ten weeks the oily layer, which showed a tendency to crystallise, was separated, and crystallised from hot alcohol. After two or three recrystallisations, about 10 g. of a crystalline substance melting at 81–83° C. was obtained, which was evidently identical with methyldiphenyltetrahydro-γ-pyrone obtained by Ryan and Devine (*loc. cit.*), and previously by Harries and Müller (Ber. (1902), **35**, 968).

Action of Alcoholic Hydrochloric Acid on Methyldiphenyltetrahydro-γ-pyrone.

The alchohol used in this experiment was prepared by boiling ordinary "absolute alcohol" with freshly-burnt quicklime under a reflux condenser for ten hours and then distilling, precautions being taken to avoid access of moisture to the apparatus by means of calcium chloride tubes.

6 g. of methyldiphenyltetrahydro-γ-pyrone were dissolved in about 700 c.c. of the dried alcohol, and the solution saturated with dry hydrochloric acid, a calcium chloride tube being attached to the exit tube of the flask. The product was allowed to stand in a tightly-stoppered flask for two days in a cool place, and as much as possible of the alcohol and hydrochloric acid removed by distillation on the water-bath. The residue was treated with two volumes of water, and thoroughly extracted with ether. The ethereal solution was washed with a dilute aqueous solution of sodium carbonate, then with small amounts of water, and dried over sodium sulphate. The ether was expelled on the water-bath, and the residual oil distilled under reduced pressure. The distillation could not be effected without some decomposition taking place, but, by conducting the operation as rapidly as possible, a viscid oil distilled at about 180–200° C./16 mm., which, when cooled and seeded with a crystal of methyldiphenylcyclopentenone prepared by the reduction of methylanhydracetonebenzil, quickly solidified. The solid was freed from adhering oil by spreading on a porous plate, and was recrystallised from light petroleum. It was then obtained as a slightly yellow crystalline solid melting at 73–75° C. The identity of this substance with methyldiphenylcyclopentenone was established by the mixed melting-point test.

Action of Benzaldehyde on γ-Benzylidenemethylethylketone in the Presence of Alcoholic Hydrochloric Acid.

A solution of 1 g. of γ-benzylidenemethylethylketone and 1·5 c.c. of benzaldehyde in 15 c.c. of concentrated alcoholic hydrochloric acid gradually deposited a solid substance, which was removed after five days. When purified by recrystallisation from chloroform and alcohol the compound melted at 157·5–158·5°, and was proved to be identical with benzylidenemethyldiphenylcyclopentenone (VI) by means of the mixed melting-point test.

One of us (J. J. L.) desires to thank the Department of Scientific and Industrial Research of the Department of Education for a Maintenance Grant, which enabled him to take part in this research.

No. 14.

ON THE STRUCTURE OF *PALÆACIS*.

By LOUIS B. SMYTH, M.A., Sc.D., M.R.I.A.,
Lecturer in Palæontology, University of Dublin.

(Plates 6, 7, 8.)

[Read November 20, 1928. Published separately January 18, 1929.]

Introduction.

The genus *Palæacis* was founded in 1860 by Milne Edwards for an organism, *P. cuneiformis*, from the Lower Carboniferous of Indiana. Since then several species, chiefly from the Lower Carboniferous, have been referred to it by various authors. It has generally been regarded as a coral, but has also been referred to the sponges. A good summary and discussion will be found in a paper by G. J. Hinde (1896).

The only specimens hitherto studied in which the structure is well preserved belong to the species *P. cyclostoma* (Phil.) and *P. humilis* Hinde. Both of these differ considerably from the type species in form, and Hinde gives good reasons for excluding the former from the genus. It will be seen in the sequel that his own species, *P. humilis*, should probably be excluded too.

Palaacis cuneiformis, the genotype, and the other wedge-shaped species which agree with it closely in form, have not hitherto been found with the internal structure sufficiently well preserved for study. Silicification has generally obscured all but the outward form. Hence discussion of the affinities of the genus has been handicapped. Records of the wedge-shaped species are sparse, and apparently they have not hitherto been found in any numbers.

It has been my good fortune to come across considerable numbers of a wedge-shaped species in the Tournaisian rocks of Hook Head, Co. Wexford. They occur at several different levels in the K, Z, and C zones. In most cases silicification has destroyed the interior structure. In this case, if the fossil occurs in shale, the external form and ornament are sometimes beautifully displayed, owing to the matrix being cleared off by weathering. But in two beds they have partially, or completely, escaped replacement, and the structure can be studied in thin slices.

The tissues turn out to be of two kinds: an inner, resembling the tissue of many typical corals; and an outer, a kind of coenenchyma, which, as far as I can find, is unlike anything hitherto described. Further, the young organism is attached to a foreign object, but, as development proceeds, the latter is gradually enveloped, and, sooner or later, completely concealed, by the growth of the outer tissue. The canal system is considerably more complex than the direct mural perforations described by Hinde.

It cannot be said that the new light on its structure brings us much closer to a knowledge of its affinities. It is too unlike any of the genera whose structure we know. There can be no reasonable doubt that it is a coral, but there appear to be no good grounds for connecting it with any of the recent perforate groups.

Palæacis has been recorded from Hook Head by de Koninck (1872) and by Etheridge and Nicholson (1878). G. J. Hinde (1896) has given a figure and brief description of a specimen from the same locality (see below, p. 131). In all three cases it has been referred without discussion to the species *P. obtusa* Meek and Worthen. I find that the Hook material must be referred to a new species.

Palæacis axinoides, sp. nov.

Palæacis obtusa L. de Koninck, 1872, p. 158.
Palæacis obtusa R. Etheridge and H. A. Nicholson, 1878, p. 221.
Palæacis obtusa G. J. Hinde, 1896, p. 446, Pl. XXIII, fig. 18.

Diagnosis. — Wedge-shaped *Palaeacis*; length and breadth approximately equal; inclination of sides approximating to 30°; the two lowest corallites, one on each lateral edge, facing outwards, with their axes making an angle of 120° to 130° with one another; the corallites reaching 5 to 6 mm. in diameter. In young coralla the third and, usually, the fourth corallites are in the same plane with the first two; in older specimens the corallites are more than one deep. Occasional specimens depart more or less from the typical form, owing to accommodation to a supporting foreign body.

Types.—Holotype in the Geological Museum of Trinity College, Dublin, T. 159/1007 (Pl. 6, figs. 1 a–c).

Paratypes in the British Museum, R. 26151 and R. 26152; and in the National Museum of Ireland, N.H. 98–1928.

The holotype and paratypes are from a thin bed of black shale in limestone, 800 yards E.N.E. of the lighthouse, Hook Head, Co. Wexford. The horizon is equivalent to the C_1 sub-zone of the Avonian.

Description.

Form.—The corallum has the form of a very flat wedge. In a typical specimen (Pl. 6, figs. 2–5), viewed normally to the plane of flattening, the outline is subcircular to polygonal. The calices occupy about two-thirds of the periphery at the thick end of the wedge. The remaining third (''lower margin'') at the thin end of the wedge is without apertures of corallites. The converging faces of the wedge (''sides'') are also devoid of apertures.

Typically the ''lower margin'' has the form of two adjacent sides of a polygon. A measurement of the angle between them (''basal angle'') in 13 specimens gave an average of 127°, with extremes at 110° and 150° (9 of them were between 120° and 130°).

Measurement of the angle of convergence of the ''sides'' of the wedge (see

Pl. 6, fig. 1b) in 15 specimens gave an average of 30°, only one (45°) being outside the limits 25° to 33°.

The greatest length of the corallum measured through the "basal angle" is usually about equal to the breadth taken from the extremities of the "lower margin" where it meets the lowest aperture on each side. The latter measurement is generally, but not always, the greatest breadth of the corallum. The largest corallum found has a length of 31 mm. and a greatest breadth of 41 mm. (Pl. 7, fig. 8).

Ornament.—The outer surface of the corallum is covered with an ornament of fine, close-set ridges, whose disposition varies much in different specimens and in different regions. They may be fairly continuous for some distance. But more often they are broken into short lengths, or even consist of rows of granules. They may be fairly straight and parallel, or sinuous, or may form a labyrinthine pattern, or a chaotic field of granules and short ridges. A parallel arrangement often occurs near the margin of an aperture and at right angles to that margin (Pl. 7, fig. 1, top), and, in general, is parallel to the axis of a corallite, and indicates its trend within the corallum. When parallel, there are from 4 to 6 ridges in 1 mm.

Corallites. — The corallites have a radial disposition diverging from the "basal angle" (Pl. 7, fig. 5), the two outermost corallites being parallel to the "lower margin" (see Pl. 7, fig. 8, where their course is evident from outside).

When less than 5 corallites are present, their apertures are usually in a single row. In other cases a longitudinal section perpendicular to the "sides" (Pl. 8, fig. 4) may cut two or more apertures.

The largest number of corallites which could be counted with certainty in one corallum was 24.

The apertures tend to be circular, but the shape is modified by the necessities imposed by the general shape of the corallum and by contact with neighbouring corallites. For instance, the lowest corallite on each lateral edge is generally trigonal (Pl. 6, fig. 1b).

The largest corallites in a corallum are usually 5 to 6 mm. in diameter, the higher figure being found in the larger coralla.

Wherever the apertures are not in contact, the surface pattern of ridges is seen on the intervening space (Pl. 8, fig. 3).

Each corallite is a deep thimble-shaped depression, without tabulae, the sides being marked by longitudinal granular septal ridges (Pl. 8, figs. 1, 2), which die out downwards, and may increase in number near the margin. The number of septal ridges per millimetre is generally between 2·5 and 3, and about 40 to 48 occur in each corallite. Irregularly spaced concentric ridges may occur on the inner wall (Pl. 8, fig. 3), or the granules on the septal ridges may be arranged in transverse rows (Pl. 8, fig. 1).

The floor of the corallite is more or less flat, and transverse or oblique to the axis of the corallite.

Pores.—The walls and floor of a corallite are perforated. On the walls the

pores occur between the septal ridges, either irregularly disposed or forming horizontal rows alternating with the transverse rows of granules mentioned above (Pl. 8, figs. 1, 7, 8).

Pores also occur in the grooves between the ridges of the outer surface. These pores, too, are irregularly distributed for the most part, but, here and there, some of them form short rows at right angles to the trend of the corallite within. They are best seen in a tangential section, and can seldom be detected by examination of the outer surface (Pl. 7, fig. 1, where the pores appear as lighter spots on the light bands).*

External tissue.—In thin slices the calcareous tissue of the corallum is seen to be of two kinds: the one forming the outer surface; the other the lining of the corallites (Pl. 7, fig. 3, and Pl. 8, figs. 4, 5).

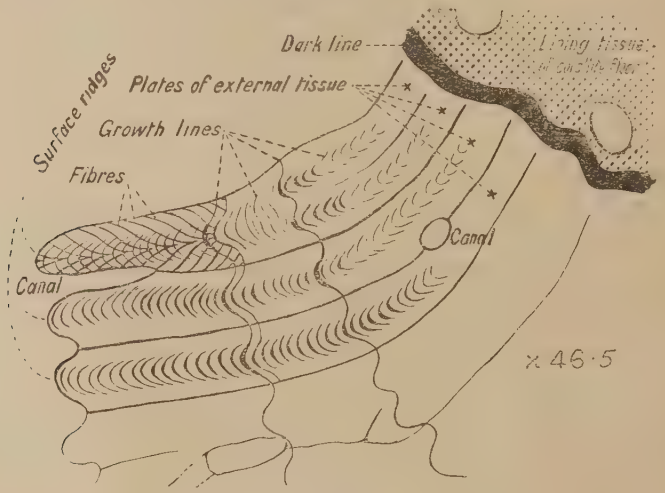


DIAGRAM OF "EXTERNAL TISSUE."

The main outlines represent a portion of Pl. 7, fig. 4. The most prominent growth lines are indicated by continuous wavy lines. Otherwise the growth lines are only represented in the median region of each plate, where, in the actual specimen, they are most distinct, and which appears as a dark band in the photograph. The arrangement of fibrous tissue has been indicated in one part of the diagram by drawing lines along the trend of the fibres. It will be noted that these lines cut the growth lines at right angles.

The "external tissue" consists of closely apposed plates, arranged at right angles to the outer surface (see Pl. 7, figs. 3, 4, and their "explanations," and text fig.). Each plate has a fibrous structure. The fibres, as they run outwards from the median plane of the plate, slope towards the outer surface of the corallum. They have a slight sigmoid undulation. The surface trace of the median plane of a plate is the median line of one of the surface ridges composing the external ornament of the corallum; the surface trace of the plane of contact of two plates is the median line of a surface groove.

* These are scarcely visible in the reproduction.

Lines of growth, *i.e.*, intersections of planes of growth by the section, are seen parallel to the outer surface, and crossing the plates at right angles (Pl. 8, fig. 4), showing that growth of this tissue took place by addition of layers to the outside. The lines of growth are wavy, representing the ridges and grooves of former outer surfaces. The fibres in the plates are perpendicular to these wavy growth lines at each point: hence their sigmoid shape. Since the surface ridges are the edges of the plates, all that was said of the form and disposition of the former (p. 127) will, of course, apply to the latter.

Lining tissue.—The tissue lining the corallites differs from that just described in not being formed of plates, but having a fibrous structure more or less at right angles to its surface. The fibres are in slightly fan-shaped groups. This tissue is thick at the bottom of a corallite, and gradually thins out upwards on the walls (Pl. 7, fig. 3). In a transverse section of a corallite the septal ridges can be seen on the inner surface of this tissue (Pl. 8, fig. 5).

Where "lining tissue" abuts against "external tissue" its boundary appears in thin section as a dark line (Pl. 7, fig. 3), usually discontinuous, and sometimes very irregular. A similar line is seen where two layers of "lining tissue" are in contact between two contiguous corallites. In the latter case, if the partition wall is thin, it is generally a simple line, with an occasional break (Pl. 8, fig. 4, top); in thicker walls it may show a herring-bone arrangement, or be represented by a zone of short curved lines, confusedly arranged (Pl. 8, fig. 5, middle).

Canals.—The pores on the inner walls and on the outer surface are the openings of a canal system. From each pore a canal ("perpendicular canal") leads into the tissue more or less at right angles to the surface, whether this be the outer surface or the walls or floor of a corallite.

In the "external tissue" these canals are excavated equally from two contiguous plates without disturbing their parallelism, and their diameter is about equal to the thickness of a plate. In the "lining tissue" the canals are, in general, larger than those in the "external tissue."

Canals opening on the floor of a corallite when traced downwards are often seen to fork (Pl. 7, fig. 3), and generally, probably always, connect up with canals from the floor or walls of other corallites.

Those opening on the inner walls of a corallite either join up with canals in the "external tissue" (Pl. 8, fig. 5, below, on the right) or go through to another corallite directly (Pl. 8, fig. 5, above the centre) or indirectly. In the last case they turn at right angles when half-way through the partition wall, where they form a two-dimensional network, which is joined by canals from both corallites (Pl. 7, fig. 2). Occasionally in a thick part of a partition wall, or in the wall bounded by three corallites, this may become a spongy tissue or three-dimensional network. When a network of canals is present in a partition wall, the "dark line" is broken up into fragments skirting the canals.

The "perpendicular canals" in the "external tissue" give off branches in its innermost layer, *i.e.*, just outside the "dark line," and also often, when the tissue is thick, at one or more other levels at different depths from the surface

(Pl. 7, fig. 9, left). These branch canals tend to be elongated parallel to the trend of the pattern of surface ridges, *i.e.*, parallel to the axis of a corallite, and may reach a considerable length and fork more than once (Pl. 7, fig. 9, below the centre). Evidently they once must have been on the outer surface, and accordingly we find them occasionally represented by grooves on the present outer surface, distinct by their greater depth from the general system of grooves of the ornament (Pl. 8, fig. 3). They strongly recall the coenosarcal grooves and astrorhizæ of certain Hydrozoa and Stromatoporoids.

Foreign inclusion.—When a section is made through the keel of the coral, a foreign body, usually a piece of shell, is found imbedded in it. In most cases this is entirely concealed in the intact coral (Pl. 8, fig. 4), but sometimes it is not completely covered (Pl. 7, fig. 7). The shell fragment is often flat and parallel with the plane of flattening of the corallum, and thus produces little or no distortion of the enveloping tissue. Slight irregularities in the included fragment become more and more masked by the thickening of the "external tissue," but many specimens are misshapen owing to their accommodation to an awkwardly shaped object.

The foreign body evidently forms the support of the young corallum. In the common case of a flat, or slightly curved, piece of shell becoming the support, the "lining tissue" of the first formed corallites is in contact with one side. Around these corallites the "external tissue" is also in contact with it. This latter, as layer upon layer is added to it, gradually extends over one side of the shell fragment, overlaps its margins, and then encroaches on the other side, creeping inwards until finally it is completely covered.

Since the elongated longitudinal canals above described are generally present in the innermost layer of the "external tissue," they may often be seen in the first thin sheet which overspreads the shell (Pl. 7, fig. 9).

Meanwhile the corallites, increasing in number, grow upwards parallel to the plane of the fragment, and soon overtop it.

In other cases the first corallite is established on the edge of the fragment, and subsequent growth is more symmetrical (Pl. 6, fig. 7, and Pl. 8, fig. 4).

The course of events can be deduced from the disposition of the growth lines of the "external tissue" seen in sections (Pl. 8, fig. 4).

Development.—The early stages of development are naturally more affected than the later ones by the form of the supporting fragment. Hence they are often very irregular. But in some cases the wedge form is exhibited at quite an early stage owing to the organism attaching itself near the edge of a small and flat piece of shell. A wedge with one concave side is frequent, owing to a small Chonetes valve having been utilised (Pl. 6, fig. 7).

At first there is a single small corallite. On its side a second corallite arises as a slight pocket formed by a portion of the edge of a new layer of "external tissue," growing outwards at that place instead of being applied to the previous layer. As its margins are raised, the bottom of the pocket becomes covered with "lining tissue." Soon the second corallite is nearly as large as

the first (Pl. 6, figs. 8, 9). As they grow they diverge from one another. In one of the angles between their apertures a third is formed in the same way as the second. As the divergence of the first two carries their apertures farther apart, the third gradually takes its place between, and in line with, them (Pl. 6, fig. 7). Similarly a fourth is developed between the third and one of the first two (Pl. 6, fig. 6).

In the stage with three, and usually in that with four, corallites, therefore, the apertures are in a single rank, as in *P. cuneiformis*, the type species. The fifth corallite is usually a little out of line with the others. With the appearance of the next few corallites there is a tendency to a zig-zag arrangement, and later the apertures may be several deep at the summit of the corallum, but are not in distinct rows (Pl. 6, fig. 1 c). In these older specimens the outer two corallites at each end of the group are usually uniserial, and are the four first formed (Pl. 6, fig. 1 b).

As a new corallite elongates, its "lining tissue" comes into contact with that of the adjoining corallites; on the outer side it is clothed with "external tissue," which grows up *pari passu* with it (Pl. 8, fig. 4, left corallite).

If the supporting fragment is relatively large, an early stage, *e.g.*, that with two corallites, has the form of round, shallow, sessile cups, with a spreading base, and strongly resembles a specimen of *Microcyathus cyclostoma* (Phil.).

We must assume that the polyps which occupied the corallites were attached to a coenosarc which secreted the "external tissue." This coenosarc, at first forming a fringe round the young coral on its supporting fragment, gradually spread until it enveloped the fragment. From that time onwards the whole coral beyond the group of polyps was coated with the coenosarc. There are specimens which seem to show that, if a polyp died, the coenosarc invaded the vacated calyx (Pl. 8, fig. 2). Multiplication took place by coenosarcal budding.

G. J. Hinde figured a specimen from Hook Head under the name *Palæacis obtusa* Meek and Worthen (1896, Pl. XXIII, figs. 18, 18 a). Through the kindness of Dr. Kitchin, I have been able to examine the original specimen, which is in the collection of the Geological Survey of Great Britain (5639, 32164–5), and find that it is undoubtedly *P. axinoides*, and almost certainly from the same bed as my specimens figured in Pl. 7, figs. 1, 3, 4, 9, and Pl. 8, figs. 4, 5. Hinde's figures are somewhat misleading, as will be seen by comparing his fig. 18 with the camera lucida outline of the same specimen given here (Pl. 7, fig. 6), in which a line joining the black dots would be vertical in his figure. The part of the specimen forming the right-hand edge of his fig. 18 is really occupied by an aperture, but the drawing and position of the figure suggest that this is not so. The deception is heightened by the incorrect representation of the surface striae as parallel to the edge of this aperture, instead of at right angles to it. Hinde says there are six calices; as a matter of fact, there are at least seven in the specimen. It is evident that he failed to recognise the lowest

one on the right of his figure. As a result, apparently, of this, the section, fig. 18 a, is neither vertical nor median, as claimed. It is a representation of the opaque surface of piece 5639. The striations on the lower and right-hand edges are the plates of the "external tissue." On the cut surface of the other piece (32164) the included shell fragment is clearly visible, whilst this latter feature and the two kinds of tissue are to be seen in a thin slice (32165). None of these points is referred to by Hinde.

Distribution.

At Hook Head *Palæacis axinoides* occurs abundantly in a few beds in the rocks correlated with C_1. Occasional specimens were found at many levels throughout Z and K, and the species is again common in a band of K age.

The state of preservation varies much. External form is best exhibited in two beds of black shale high in C_1, where the specimens are highly silicified and their internal structure much defaced. From the upper of these beds were chosen the holotype and paratypes. The minute structure of the skeleton was chiefly worked out on material in dolomitic limestone from the base of beds equivalent to the C_1 "*laminosa* dolomite." Specimens from the K level have the internal structure fairly well preserved too.

Besides the occurrences just mentioned, a form of *Palæacis* with marked peculiarities is fairly common at two horizons in the highest part of the exposure (*Chonetes* beds = top of C_1, or higher). With three exceptions, amongst forty in which the point could be observed, the specimens collected here consisted of two corallites only, without any trace of a third (Pl. 6, figs. 10, 11). The base rarely shows any irregularity that could be due to a supporting fragment, and in cases where specimens were sectioned no such foreign body could be demonstrated. In many specimens, owing to the thinness of the external tissue, the contours of the component corallites can be made out, and the base of the older projects downwards farther than that of the other one, from which it is separated by a slight notch (Pl. 6, figs. 10 a, b, g, i). The apertures, too, may have a notch between them. In one specimen the latter feature is extreme (Pl. 6, fig. 10 c). The two corallites have become much elongated without any others having been developed to fill the space left by their divergence. Only one such specimen was found, and it cannot be looked upon as characteristic.

Are the forms from these beds to be regarded as a distinct species? I am inclined to think not. The structure is essentially the same as in young specimens of the typical form. Of the three exceptions mentioned above, one has a well developed third corallite (Pl. 6, fig. 12); the other two an incipient but distinct one. A couple of specimens exhibit an irregular concavity at the base (Pl. 6, figs. 10 f, h), possibly due to a supporting fragment subsequently removed by solution. Silicification obscures the internal structure, and it seems possible that minute foreign bodies may have escaped notice in sectioning. One or two young specimens from the lower horizons approximate to the regularity of form here characteristic.

Probably the peculiarities are a response to unfavourable environment; the remaining fauna of these beds is distinctly dwarfed, and here, too, in the case of *Vaughania vetus* (Smyth, 1927) only young stages were found.

Percival (1876) reported *Palæacis cuneata* (Meek and Worthen), (= *P. cuneiformis* M.-Ed.) from the neighbourhood of Bristol. I have examined some of his material to see if it might be the same as the Hook form. Two specimens from Kingsweston Down are distinct from *P. axinoides*, and Percival's identification appears justifiable. A specimen (Brit. Mus. R. 2697), from Henbury, appears to agree with the two-corallite stage of *P. axinoides*, and another (R. 2698), from Middlehope, near Woodspring Priory, agrees perfectly with that shown in Pl. 6, fig. 12, of this paper. Some more mature specimens from Henbury (R. 2696, R. 22558–66) appear to be distinct from *P. axinoides*, and approach *P. cuneiformis*.

Discussion.

The genotype of *Palæacis* is *P. cuneiformis* Milne-Edwards (1860, vol. iii, p. 171, Atlas, Pl. E 1, fig. 2). The same species was described and figured from the same locality under the name *Sphenopoterium cuneatum* by Meek and Worthen (1860, p. 447; 1866, p. 145, Pl. 17, figs. 1, 2). *Palæacis axinoides* agrees with the genotype in its general form, external ornament, septal ridges, and arrangement of pores on the outer surface and on the calyx wall. Milne-Edwards mentions a finely vermicular coenenchyma. Certain other investigators have rejected this character (Kunth, 1869, p. 185; Hinde, 1896, p. 443). If, however, the present species is correctly referred to this genus, the description is justified, for the external tissue might be described as a coenenchyma, and the ornament is in places quite vermicular.

Unfortunately the minute structure of the type species is so little known that it cannot be determined whether it possesses an "external tissue," a canal system, or included foreign body such as occur in *P. axinoides*, but the observations hitherto published are not incompatible with their existence.

Taking into consideration the great resemblance in ascertainable characters and the absence of observations definitely excluding it, it seems justifiable to place the new species in *Palæacis*.

P. cuneiformis differs from the new species in the following particulars: the sides are more nearly parallel; the length is distinctly greater than the breadth; the corallites are strictly in one plane; the two outermost corallites are inclined to one another at a smaller angle, and their apertures are much more elevated above the lowest point of the keel; the apertures of the corallites are separated by an interval in which the surface pattern is continued from one "side" to the other.

If the new species is correctly referred to *Palæacis*, the additional knowledge of the structure of this genus confirms the exclusion of *Microcyathus cyclostoma* (Phil.), as suggested by Hinde (1896, p. 447), but will also exclude Hinde's species, *P. humilis*, which is "without any trace of attachment," has "no

indications of granulations, tubercles, or septa'' in the calices, and ''neither epitheca nor coenenchyma is present'' (1896, p. 441).

Judging by the form and surface ornament, it is probable that the following species, in addition to the genotype, belong to *Palæacis*:—*Sphenopoterium obtusum* Meek and Worthen (1860, p. 448; 1866, p. 233, Pl. 17, figs. 2 a–e), including *P. cymba* von Seebach and *P. umbonata* von Seebach (1866, p. 309, Pl. IV, figs. 3, 4); *Palæacis bifida* Weller (1909, p. 277, Pl. 10, figs. 5–11); *Palæacis compressa* de Koninck, non Meek and Worthen (1872, p. 158, Pl. XV, figs. 7, 7 a).

Palaeacis obtusa (M. & W.) differs from *P. axinoides* in the greater angle of inclination of the ''sides,'' the larger apertures, and the cruciform disposition of the apertures of the first four corallites. To this species the Hook Head form was referred by de Koninck, Etheridge and Nicholson, and Hinde (see p. 126).

P. bifidus Weller is extremely like the two-corallite stage of *P. axinoides*, but is not so compressed.

De Koninck describes and figures a form under the name *P. compressa* which does not appear to me to agree at all with Meek and Worthen's description or figures of their species. It has, however, a general structure like the Hook species, but is more loosely built. The greatest resemblance is in the two-corallite stage.

The classification of *Palæacis axinoides* must at present remain an open question, in view of the unique structure of the external tissue. The surface ornament recalls *Microcyathus* Hinde (1896, p. 447; Eth. & Nich., 1878, Pl. XII, fig. 4), *Vaughania* Garwood (1912, p. 564; Smyth, 1927, Pl. XX, fig. 1), *Trachypora* Frech (1885, p. 107, Pl. IX, fig. 5), and *Trachypsammia* Gerth (1922, p. 13, Pl. II, figs. 6–9). The first two of these, however, differ widely from *Palæacis* in their other characters; the last two are not sufficiently well known for comparison.

What was the mode of life of *Palæacis axinoides*? It appears to have been attached when young, but later the whole corallite was enveloped in coenosarc, and therefore free. In these respects we may compare it with the recent solitary genus *Fungia*, which, when young, is attached by a short stalk, but in the adult condition is free, the body wall covering the whole under surface of the corallum. *Fungia*, however, is wide and depressed, and therefore capable of standing stably: *Palæacis* is high and narrow, with a keel-like base, and it is not easy to conjecture how it lived in the free state.

Its wedge-like shape recalls the recent Eupsammid genus *Endopachys*, though this is a solitary form. It further resembles *Palæacis* in being perforate, and in being attached to a foreign body when young, and free when adult.

Freedom is, however, gained by fracture, and not by enveloping its support. It seems probable, from the three points of resemblance enumerated, that the mode of life of these two corals may have been somewhat alike, and information on the natural history of *Endopachys,* which seems to be lacking, may throw light on the conditions to which *Palæacis* was adapted.

It is hard to believe that the keel was stuck in the mud, since the apertures of the two lateral corallites are so slightly elevated above the lowest point of the keel. The comparatively heavy skeleton precludes the possibility of a pelagic life.

The enveloping of the supporting body is paralleled in the case of *Heterocyathus,* one of the recent Turbinoliidæ. This coral attaches itself to a small Gastropod shell, which it subsequently surrounds. In this case the matter is complicated by the fact that it is always a shell containing a Gephyrean worm, which is supposed to keep the coral in the upright position.

I am greatly indebted to Dr. W. D. Lang and to Dr. F. L. Kitchin for the loan of specimens under their charge for purposes of comparison. Also to Dr. Stanley Smith for a loan from his private collection.

DETAILS OF LOCALITIES REFERRED TO IN THE EXPLANATIONS OF PLATES.

Locs. 13 b and c, 500 yards S.S.W., and 12 c, 250 yards S.E. of Slade Castle, Hook Head, are in the *Chonetes* beds, which form the highest part of the Hook exposure. The horizon is not lower than the top of C_1.

Locs. 14 y and 16 z are two exposures of the same bed of black shale, the former 800 yards E.N.E. of the lighthouse at Hook Head, the latter immediately to the W. of the lighthouse, and N. of a gully which runs under it. Its horizon is C_1.

Loc. 19 c is 950 yards N.N.W. of the lighthouse at the base of the dolomite band = *laminosa* dolomite, base of C_1.

Loc. 3 h is at the S. point of Woarwoy Bay, $2\frac{3}{4}$ miles N.E. of the lighthouse, and of K age.

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EXPLANATION OF PLATES.

The reference numbers, unless otherwise stated, are those of specimens in the Geological Museum of Trinity College, Dublin. The symbols denoting localities are explained on p. 135. Magnification is indicated on the plates.

Plate 6.

Palæacis axinoides, sp. nov., from Hook Head.

A black dot is centrally opposite the aperture of the lowest corallite on each side.

Fig.

1. Holotype, *a* from the side, *b* from the end, *c* from above. The cross indicates the same corallite in each case. T. 159/1007. Loc. 14 y.

2–5. Typical specimens, natural size. Fig. 5 has seven corallites; fig. 4, only six. Fig. 2, F. 160/1007; loc. 14 y. Fig. 3, F. 161/1007; loc. 16 z. Fig. 4, F. 162/1007; loc. 14 y. Fig. 5, F. 163/1007; loc. 14 y.

6. Young specimen, with four corallites, arranged in a single row, and a bud. F. 164/1007. Loc. 14 y.

7. Three-corallite stage on the cardinal edge of *Chonetes* cf. *hardrensis*. F. 165/1007. Loc. 14 y.

8, 9. Two specimens in the two-corallite stage, each seen from three aspects. 8 b and 9 b show the supporting shell fragment not yet covered. Fig. 8, F. 166/1007; fig. 9, F. 167/1007; both from loc. 14 y.

10. Camera lucida outlines of two-corallite specimens from the Chonetes beds, locs. 12 c and 13 b. Fig. 10 f has the bud of a third corallite. Numbered in order from F. 168/1007 to F. 176/1007.

11. A very symmetrical two-corallite specimen from the same beds. F. 177/1007. Loc. 12 c.

12. A three-corallite specimen from these beds. F. 178/1007. Loc. 13 c.

PLATE 7.

Palæacis axinoides, sp. nov., from Hook Head.

Fig.

1. Tangential section in the "external tissue" just beneath the surface ornament. The canals appear as white spots on the light bands.* The top right-hand edge is the margin of a corallite. F. 179/1007. Loc. 19 c.

2. Longitudinal sections of walls formed by direct contact of "lining tissue" of adjacent corallites. F. 180/1007. Loc. 3 h.

3. Section which cuts the upper corallite nearly longitudinally, and shows forking of canals in the "lining tissue." A second corallite below is cut nearly transversely through the "lining tissue" at its base. In the latter the black spots are canals; the smaller lighter spots the centres of fan-like groups of fibres. A third corallite is grazed on the right. The dark line between the two kinds of tissue is visible. F. 181/1007. Loc. 19 c.

4. A portion of the "external tissue" of fig. 3 more highly magnified. Each plate has a dark centre and a light border. The junction between two plates appears as a faint line along the middle of a light band. To make the matter clearer, two of these junctions have been emphasised, and thus one plate has been outlined. A portion of a wavy growth line has also been strengthened. F. 181/1007. Loc. 19 c.

5. Camera lucida sketch from an opaque surface of a nearly median section in the plane of compression. A ribbed shell fragment is present. F. 179/1007. Loc. 19 c.

6. Camera lucida outline of the specimen from Hook Head sectioned and figured by G. J. Hinde (1896, Pl. XXIII, fig. 18). The dark vertical line is an incipient saw-cut. A line joining the black dots would be a vertical line in Hinde's figure. This specimen is in the collection of the Geological Survey of Great Britain, 32164 and 5639.

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* See footnote, p. 128.

7. A fairly large specimen, in which the foreign body has not been completely covered. F. 182/1007. Loc. 14 y.

8. The largest specimen found. F. 183/1007. Loc. 16 z.

9. A thick section in the plane of compression of a three-corallite specimen photographed by transmitted light. The two dark patches are parts of the foreign body. Long branched canals are seen in the external tissue in contact with the foreign body (centre), and parallel to the outer surface (left). F. 184/1007. Loc. 19 c.

Plate 8.

Palæacis axinoides, sp. nov., from Hook Head.

Fig.

1. The nearer walls of two corallites have been broken away, giving a good view of the pores on the inner wall (left) and the septal ridges (above). F. 185/1007. Loc. 14 y.

2. The granular nature of the septal ridges is seen on the left; on the right "external tissue" has invaded the calyx, probably owing to the death of the polyp. F. 186/1007. Loc. 16 z.

3. Another view of the same specimen to show the "coenosarcal grooves." There are 7 or 8 of them in a row below, and to the left of, the apertures.

4. Longitudinal, nearly median section, transverse to plane of compression, showing the growth lines in the "external tissue" and their relation to the corallites and to the foreign body (the thick white streak below). F. 187/1007. Loc. 19 c.

5. Another section of the same specimen parallel to the first, cutting one of the lateral corallites (below) nearly transversely, and showing sections of the septal ridges on the "lining tissue."

6. A bud forming in the angle between two apertures. F. 188/1007. Loc. 16 z.

7 and 8. Weathered fragments, showing the relation between the pores and septal ridges. Fig. 7, F. 189/1007; loc. 14 y. Fig. 8, F. 190/1007; loc. 16 z.

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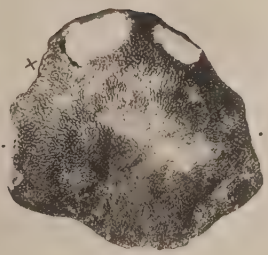

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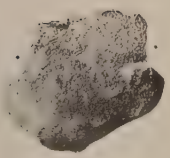
1c x2



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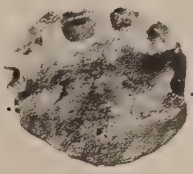

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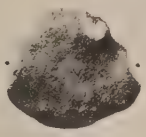

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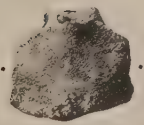

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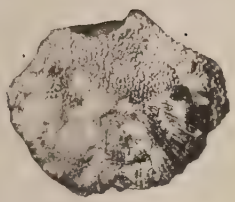
5 x1



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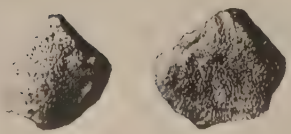
8a



9a

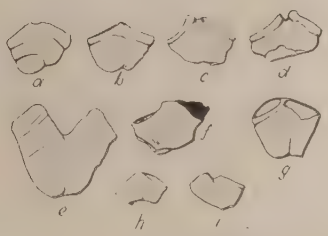
8b

9b

8c

9c

x3



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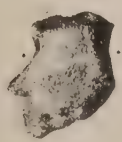

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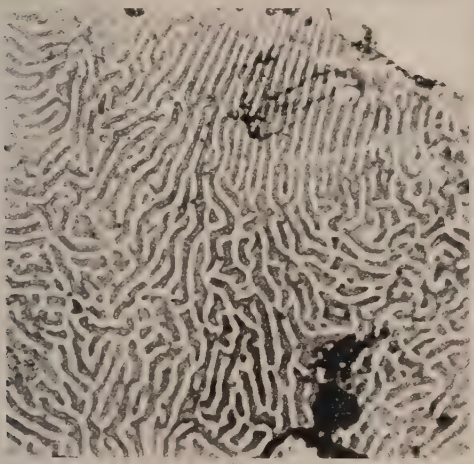

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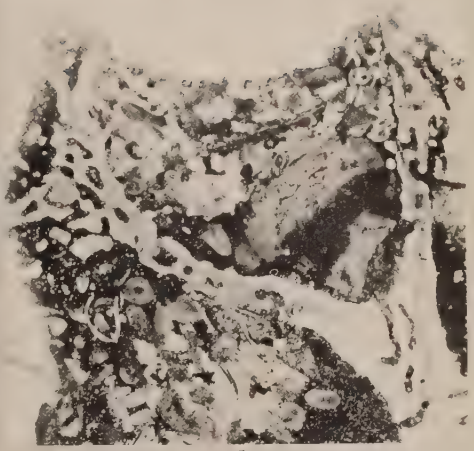

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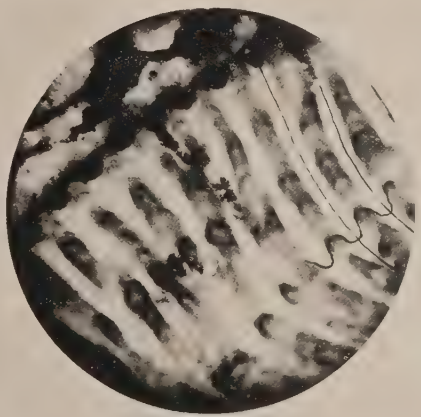
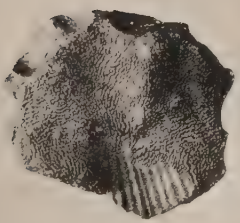
3 × 3



4 × 32

5 × 1

6 × 1



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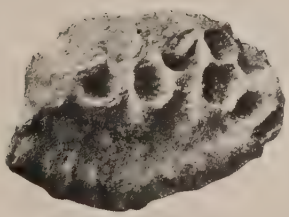

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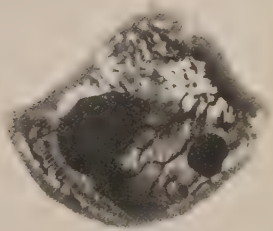

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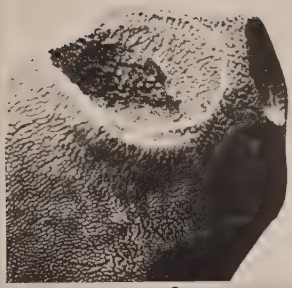

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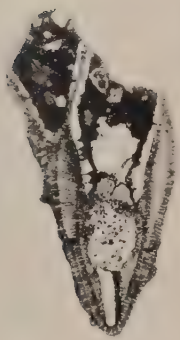

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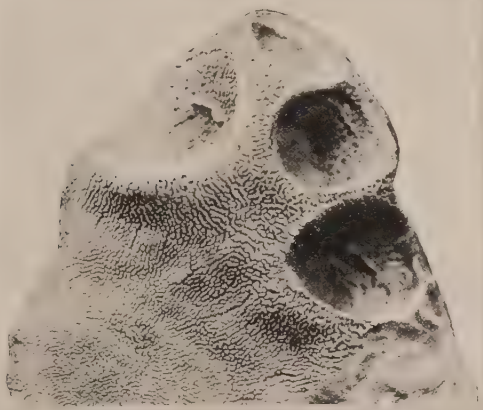

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No. 15.

WILLIAM HIGGINS, A PIONEER OF THE ATOMIC THEORY.

By J. REILLY, M.A., Sc.D., M.R.I.A.,

AND

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Introduction.

In the standard histories of chemistry we find occasional references to a controversy between John Dalton, the author of the Atomic Theory, and William Higgins, an Irishman, whose name is strange to most students of chemistry outside this country. Higgins claimed that he had enunciated the theory previous to Dalton. Von Meyer's comments on the subject are as follows:—

"Higgins certainly expressed opinions which, on a superficial glance, appeared similar to those of Dalton, stating, as they did, that the smallest particles combine in simple numerical proportions to form chemical compounds. But these views were brought forward without any internal organic connection, and, moreover, they were not founded on experiment" ("Hist. of Chemistry," p. 110). Most of the other references in the general literature of the history of chemistry are similar to the above.

The authors well recognise the futility of attempting to rekindle the long-dead embers of such a controversy. But it must be borne in mind that the atomic theory cannot be regarded as anyone's sole preserve. It is the work of many minds—a gradual evolution from the atoms of Leucippus and Lucretius, and the hard, massive particles of Newton, to the fruitful hypothesis of the nineteenth century. The object of this paper is to fix the true place of William Higgins in that evolution, to see how far his views helped in the formulating of the theory, and to attempt to obtain for him any credit that he may deserve.

Biographical Sketch.

William Higgins was born in the county of Sligo. The exact year of his birth is unknown, but from some evidence in his writings it may be taken to be 1766 approximately.

He was the nephew of Bryan Higgins, M.D., a physician who had a big and well-deserved contemporary reputation as a chemist. The younger Higgins

was taken to London as a youth, and trained in chemistry by his uncle, in his school in Greek Street, Soho; this school, in addition to being one of the best in existence at the time, supplied refined chemicals to scientific workers. Among its many customers was Priestley. It is of interest to note that on one occasion an over-zealous friend of Bryan Higgins, Dr. Brocklesby, charged Priestley with passing off as his own experiments which he had seen in the Greek Street school. When approached on the matter, Bryan Higgins supported the charge, though not over-enthusiastically. He carned in reply a pamphlet which may still be read with interest as a tribute to Priestley's gifts as a pamphleteer.

It is certain that William Higgins obtained in his uncle's school a training in chemistry second to none, and when he entered Pembroke College, Oxford, he was better fitted as a student than most of his fellows. That his abilities were recognised at the University is evident from his appointment as demonstrator to Dr. Beddoes, whose lectures on chemistry attracted the largest classes in the University for five hundred years.

After graduation he left the University and worked again with his uncle. In 1789, as a young man, he published his first and most important work, "A Comparative View of the Phlogistic and anti-Phlogistic Doctrines." This work was a reply to Kirwan's "Essay on Phlogiston," and on it rests Higgins' claim to a place of honour in the development of the atomic theory. Despite unfavourable circumstances, the book had a considerable measure of success, being the first, and probably the best, contemporary defence of the anti-phlogistic doctrine in the English language. At the time of its publication more than one thousand copies were sold, and it ran into two editions.

About the time of the publication of this book, Higgins' relations with his uncle became somewhat strained. This might have been expected when the nephew, and quondam pupil, became one of the first and warmest supporters of the anti-phlogistic doctrine, of which the uncle and teacher was, at that time, an uncompromising opponent. He left his uncle, and lived for a time in straitened circumstances. In 1791 he was appointed Superintendent to the Apothecaries' Hall, Dublin, to raise the quality of pharmaceutical products, at a salary of two hundred pounds a year, apartments, coal, and candles. About three years later he was appointed to the Royal Dublin Society, on the recommendation of Kirwan, his former antagonist. In 1800, by one of the last Acts of the Irish Parliament before the Union, a number of professors were appointed to the Society, and he became Professor of Chemistry and Mineralogy. This post he retained till his death in 1825. During his years in Dublin he devoted himself to technical and applied chemistry.

In 1799 he published an "Essay on the Theory and Practice of Bleaching," wherein sulphuret of lime is recommended as a substitute for potash. In the preface to this work (p. ix) he writes: "I have seen with pleasure, that since the controversy" (the phlogiston controversy) "was laid aside, and the true theory of chemistry adopted and fixed upon a firm basis, most chemical philosophers have applied their talents to the improvement of the arts and manufactures, which is the ultimate and grand object of the science."

Like his uncle, he was very keen on disseminating the knowledge he had gleaned by experiment and speculation, and delivered largely attended and highly popular series of lectures in Dublin. In 1806 he was elected a Fellow of the Royal Society, but never attended its meetings. For biographical details of the life of Higgins, see "Dublin Quarterly Journal of Medical Science," New Series 8, p. 487, and Meldrum, "New Ireland Review," **31**, 1909–10, pp. 275 and 350.[1]

Higgins' Charges against Dalton.

In dealing with the controversy which is the main interest of this paper, it is better first to understand clearly how far Higgins claimed priority to the atomic theory of Dalton. At first he seems to have taken no action till others began to make claims for him. Then, in 1814, he published a work entitled "Observations and Experiments on the Atomic Theory and Electrical Phenomena." In this work he makes his case, reprints the salient features of his earlier work, and compares it with Dalton's. The following quotation from this work will give a pretty clear idea of his claims. Writing of the circumstances that led up to the publication of his earlier work, he says (p. 7):—

"When I commenced my investigations of chemical theory in 1788 and 1790, at which time the work was sent to press, all the chemical philosophers of Great Britain, Sweden, Germany, Ireland, Holland, and Italy, and most of those in France, were phlogistians. Under these circumstances a very young man, such as I was at the time, might well be intimidated, and even deterred from offering an opinion on the subject of chemical philosophy; however, the new views which I had fortunately adopted furnished me with some degree of confidence.

"I was very well aware of the importance as well as of the difficulty of the task which I proposed to myself. I had to frame a new system of investigation, in order to explore two doctrines that were at the time doubtful and obscure.

"I own it cost me many weeks, nay, many months, of anxious meditation and study before my plan was perfectly formed. At length it occurred to me that chemical attraction only prevailed between the ultimate particles of simple elementary matter, and also between compound atoms. The play of chemical affinities between these divisions was therefore only to be attended to.

"These considerations gave birth to that doctrine which Mr. Dalton, eighteen years after I had written, claimed as originating from his own inventive genius. What his pretensions are will be seen from the sketches which will soon follow, and which have been taken from my book.

"In the application of my system to chemical theory I expressed by numbers

[1] The authors would be thankful for information regarding any sketch or drawing of William and Bryan Higgins, as they desire, if possible, to include a copy in their book on Irish Chemists, now in preparation. Dr. Sullivan refers to a sketch of Bryan Higgins in his memoir in the Dub. Quarterly J. of Med. Sc.

the relative forces of attraction existing between the different kinds of ultimate particles and atoms of matter to each other. This was of infinite use to me during my researches, and if followed up would mature the science into that mathematical precision in which it is at present deficient.

"This I consider as one of the most important features of the system; it has not even been mentioned by Mr. Dalton in his work, and when he repeats experiments formerly made by me, he does not even glance at the source from whence he derived his information. Mr. Dalton has represented the ultimate particles of elementary matter by means of symbols, and atoms are represented in the same way, with the proportion of their elementary constituents.

"These signs correspond with my diagrams, except that numbers expressive of the relative forces of attraction are left out; these symbols, I own, shew some ingenuity; they are, excepting the omission of the numbers, preferable to my diagrams.[2] This can only be considered a mechanical improvement. Definite proportions are also represented by these symbols, and the same is strictly attended to by my diagrams. Specimens of both will be exhibited hereafter. The relative weights of the different particles of elementary matter, that of hydrogen being a standard, have also been given by Mr. Dalton. I have done the same in many instances. After this the relative weight of compound atoms could readily be conceived.

. . . . . .

"I was the first who attempted to ascertain the relative weights of the ultimate particles of matter, as shall be proved hereafter.

. . . . . .

"The atomic doctrine has been applied by me in difficult and abstruse researches. Its application by Mr. Dalton has been in a general and popular way, and it is from these circumstances alone that it gained the name of Dalton's theory. Mr. Dalton's work is read; mine had been laid aside as soon as the controversy which gave rise to it ceased; and at that time the theory in question was not understood, nor did I expect it would be for a considerable time. I calculated upon the middle of the present century. Probably it would have lain by since if it had not been for the genius and industry of Mr. Dalton."

The above extract gives a very clear idea of the claims Higgins made against Dalton. It may, however, be said in comment that there is no evidence available to show that Dalton did plagiarise Higgins, though, as Higgins himself, and almost everybody who has touched the subject since then, have said, it is rather strange that Dalton overlooked such an important contribution to the science as Higgins' earlier book, more particularly in view of the familiarity with it displayed by so many eminent contemporary chemists. In justice to Dalton, however, the reader should be reminded that his early training was as a

[2] Higgins' diagrams approximated in some measure to the later Berzelian system of nomenclature.

mathematician and physicist, rather than a chemist. In this connection Roscoe and Harding ("New View of Dalton's Atomic Theory," p. 50) write:—

"There seems to be no doubt that the idea of atomic structure arose in Dalton's mind as a purely physical conception, forced upon him by the study of the physical properties of the atmosphere and other gases."

From the physical considerations he was led to the chemical interpretation, and not *vice versa*, as Thomson would have us believe. Under these circumstances his ignorance of Higgins' work can be easily understood.

However, the fact that it cannot be proved, or indeed is not claimed, that Dalton plagiarised Higgins, in no way prejudices the claim that Higgins anticipated Dalton in many details. The atomic theory was a gradual growth; sooner or later someone was bound to collect the scattered threads of chemical theory, and attempt to unify them on an atomic basis. Both Higgins and Dalton attempted to do so. Dalton's work fell on fruitful soil under favourable circumstances; Higgins' was done at a time when one of the few unifying principles of early chemistry, the phlogiston theory of combustion, was fighting for its existence after a long reign of more than a century. In the turmoil Higgins' work bore no fruit. Had it been followed up, and the errors inherent in it eradicated, as the errors in Dalton's were, it might easily have led to a very complete enunciation of the theory many years earlier.

One other remark may be made with advantage on this phase of the subject. From what is known of Higgins, he was by no means the type of man that would willingly seek such a quarrel. From such scanty biographical details as remain, he would, one thinks, be very slow to take up cudgels without reason. Throughout his works he puts forward his views with a refreshing modesty, and is always ready with the source of observations that are not original.

It seems most likely that over-zealous friends at first put forward his claims, and probably exaggerated them, without any part being taken in the agitation by Higgins himself, just as in earlier days his uncle, Bryan Higgins, was led into controversy with Priestley. Later on, roused by the counter-charges his friends' criticisms had brought about, and the studied ignoring of his work by some contemporary compilers, he was goaded into reply.

Higgins' Main Work, "A Comparative View of the Phlogistic and Anti-Phlogistic Doctrines."

The first edition of Higgins' main work, his "Comparative View," was published in 1789. It had been in preparation for about two years previously. For a proper understanding of this work it is essential to refer it to its background, to be familiar with the main currents of chemical thought of the period in which he wrote.

The main, indeed the only, unifying principle of early chemistry which had any considerable success was the phlogistic hypothesis of Becher and Stahl. To this most chemists were still clinging rigidly. Up to that time chemistry had been almost entirely qualitative, and the utter neglect of quantitative

relations had made it possible for chemists to believe implicitly in a doctrine bristling with contradictions.

Lavoisier had by 1777 convinced himself that the phlogistic hypothesis was not merely untrue, but, also a distinct handicap to the science, yet he was not sufficiently sure of his ground to make any open attack on the system. In his earlier works he simply ignored it, and it was not till 1783 that he made any formal attack on it. Outside France the leaders of chemical thought clung inflexibly to the theory. England, in particular, was the stronghold of the phlogistians. Joseph Black (1728–1799), Henry Cavendish (1731–1810), Joseph Priestley (1733–1804), and Richard Kirwan (1733–1812) were then all phlogistians; Black and Kirwan, however, acknowledged the logic of the Lavoisierian doctrine before their deaths.

William Higgins' work was a bold defence of the anti-phlogistic doctrine, and the first in the English language. It was written expressly in answer to Kirwan's "Essay on Phlogiston." That such a work would not be very popular in chemical circles is evident. Even his uncle, Bryan Higgins, from whom he had learned most of his chemistry, and to whose instruction he owed his first acquaintance with atoms and molecules, was prejudiced against it. It was, in fact, the direct cause of an estrangement between them.

That Higgins fully recognised the prejudice that existed against his view-point is evident throughout his work. In his introduction to it he writes (p. 11):—

"Although I adopted the anti-phlogistic doctrine four years ago, and although every phenomenon which occurred to me since tended to confirm the truth of that doctrine, yet, when I considered the number of able philosophers—Priestley, Kirwan, Black, Higgins, etc.—who persisted in the old doctrine, I began to waver in my principles, and my desire to minutely inquire into both doctrines daily increased; but, knowing how inadequate I was to such an arduous task, and likewise how many there were who might have performed it so much better than myself, it was some time before I could summon resolution enough to begin; but my attachment to the science at length overcame every other consideration.

"If my efforts in this enlightened age be too feeble to do much good, I hope at least that they will not be productive of evil. I have written with conviction and without prejudice (otherwise it would be natural to suppose that I would join my countrymen in defence of that doctrine in which I have had my early instructions in chemistry). If I should be so unfortunate as to reason upon wrong principles, the sooner I am contradicted the better pleased I shall be. But if my arguments and inductions be just, if I even should meet with censure, it cannot last long; time, the parent of truth, will operate in my favour."

One fact which must be borne in mind in dealing with Higgins' work is that its immediate object was the defence of the anti-phlogistic doctrine, and that his views on the atomic theory are used more as a method of reasoning

to enable him to overthrow the more easily his opponents' cause than for their own sake. That is one of the main reasons why his work was neglected by contemporary chemists. In Dalton's later work the atomic theory was his main end in view. He heaped up evidence in favour of it, and enunciated it openly. Higgins, on the other hand, was primarily interested in the phlogiston theory, and he used the atomic theory as a convenient, but nevertheless secondary, method of reasoning. The principles which Dalton openly enunciated in 1808 Higgins tacitly assumes and uses throughout his work of 1789.

It consisted of a Preface and ten Sections as follows:—

I. Of the Composition and Decomposition of Water.
II. Of the Composition of Acids.
III. Of the Vitriolic Acid.
IV. Of the Nitrous Acid.
V. Of the Marine Acid.
VI. Of the calcination of metals, via sicca.
VII. Of the calcination of metals by steam, and the decomposition of water.
VIII. Of the reduction of metallic calces by charcoal, and the formation of fixed air.
IX. Of the solubility of metals.
X. Of the precipitation of metals by each other.

Of these, Sections III and IV, on the Vitriolic Acids and Nitrous Acids, are the most important to the student of atomic chemistry. The other chapters, notably those on the composition of water and of acids, are of interest for the clarity of the views expressed, which, in several instances, are distinct improvements on the current opinions of philosophers of the eminence of Priestley, Cavendish, and Kirwan. It is also of interest to note in them Higgins' familiarity with the experimental side of the investigations, and the number of original experiments he quotes. Throughout his work he lays great stress on experimental work, and it is hard to understand the strictures of those who dismiss him as a mere speculator.

The Fundamental Physical Concepts of Dalton's Atomic Theory.

In assessing the value of Higgins' work on the atomic theory, it is essential to compare his work with Dalton's. The latter first made his work available to the public in his "New System of Chemical Philosophy," published in 1808. Previous to this it was known only to that particular section of the chemical world in direct touch with him and his lectures. In 1807 Thomas Thomson, in his "System of Chemistry," gave a short account of the theory (vol. iii, pp. 424–9 and 451–2). This was the first public exposition of the work which made it available to a large circle of readers. The author states that the sketch he gave "was derived from a few minutes' conversation, and from a short written memorandum."

Dalton's earlier work—mainly papers read before the Manchester Society—contains very little bearing directly on the atomic theory. Reading them in conjunction with his "New System," we can catch here and there glimpses of his later brilliant exposition, and follow in some measure the growth and development of the theory in his mind. None of these earlier papers, however, contain any amount of atomic philosophy comparable with that in Higgins' "Comparative View"—a fact which makes it all the more to be regretted that Higgins did not follow up such a promising beginning.

An impartial reader cannot doubt that Higgins' work contained the fundamental germs of the atomic theory, and that with it as a starting-point atomic theory would have progressed to its present standard had his views been adopted in 1789. Circumstances led to the neglect of that work, and it is to the genius and industry of Dalton, and the encouragement and friendly criticism of his contemporaries, that the main credit for the establishment of the theory must be ascribed.

The following quotations from Dalton's work will give a clear idea of his conception of atomic chemistry, and serve as ready touchstones to which to refer Higgins' work for comparison :—

(1) "All bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction" ("New System," p. 141).

(2) "The ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc." (p. 141).

(3) "When any body exists in the elastic state, its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity, or otherwise, are disposed to encroach upon it, at a respectful distance" (p. 211).

(4) "Chemical Analysis can go no farther than to the separation of particles one from another, and to their re-union. No new creation or destruction of matter is within the reach of chemical agency" (p. 212).

(5) "In all chemical investigations it has been justly considered an important object to ascertain the relative weights of the simples which constitute a compound. But unfortunately the enquiry has terminated here, whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and guide future investigations, and to correct their results. Now it is one great object of this work, to show

> the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one compound particle'' (p. 215).

The above extracts give, in Dalton's own words, the fundamentals of his atomic theory as he conceived it. From this skeleton, aided by the work of Gay-Lussac, Avogadro, Berzelius, and many others, the atomic theory has risen to its present state. We will now see how the fundamentals of Higgins' work compare with the above.

Higgins' Atomic Concepts.

The first three extracts from Dalton give his views on the ultimate state of matter. Number one is merely a re-statement of the fundamental atomistic doctrine, which can be traced back to Leucippus, and his pupil and associate Democritus. It is a conception common to a great deal of scientific literature from the earliest times.

This conception of the atom or ultimate particle as the indivisible unit in the constitution of matter persisted in philosophy, and was the immediate source of Dalton's first proposition. Higgins assumes the same thing throughout his work; he probably learned his first lessons in atomics from his uncle, Bryan Higgins, who throughout his work regards matter from the Newtonian standpoint. This, of course, is by no means unusual in the writings of the time.

Dalton's views on attraction and affinity were commendably simple. He deserves great credit for the way in which he confined his hypotheses to what was immediately necessary. Higgins, on the other hand, advanced his speculations on attraction beyond that point. In addition to assuming the atomic conception of matter, he attempts to define the attraction, which Dalton very wisely left alone, in mathematical terms. Throughout his work it will be noted that he is very keen on interpreting his results as mathematically as possible. He gives figures for the affinity of various substances for one another. Exactly how these figures were arrived at he does not explain very lucidly, but it is apparent that the main principle involved a consideration of their affinity for oxygen as expressed in Lavoisier's table.

Thus, to charcoal (carbon), near the head of the table, he ascribes an attraction for oxygen of 10. Iron, a little lower down, is rated 7. Sulphur, still lower, $6\frac{7}{8}$, hydrogen $6\frac{5}{8}$, and so on. In his diagrams of molecules, he attempts to include, in addition to a representation of the atoms concerned, a representation of the forces by which they are drawn together. Thus Dalton expresses his atom of water diagrammatically as ⊙ ○ where ⊙ is an atom of hydrogen and ○ one of oxygen. Higgins attempts to go further, and gives his molecule of water as I $\frac{6\frac{5}{8}}{}$ D. "I" represents an atom

of hydrogen (inflammable air); "D" an atom of oxygen (dephlogisticated air), and the $6\frac{5}{8}$ represents the aggregate attraction binding the two atoms.

In each case the verbal interpretation of the symbols is identical.

Dalton gives "an atom of water, or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat" ("New System," p. 219). Higgins gives "water is composed of molecules formed by the union of a single particle of oxygen to a single ultimate particle of hydrogen" ("Comp. View," p. 36).

The representations of other molecules differ in the same way. Higgins used these notions of the constitution of compounds as a basis for his work, and, by means of his mathematical expressions for affinity, attempts to explain many current problems—e.g., why a metal dissolves in dilute sulphuric acid with the evolution of hydrogen, when it will not dissolve in the cold in either water or the concentrated acid. His explanations on this basis are very novel and ingenious. His attempts to place the science on a mathematical basis are very praiseworthy, but such an attempt was hopelessly premature and beyond the scope of the time. He was very prone to try to put too much into his work, and undoubtedly the complication of his diagrams by the somewhat mysterious expressions of affinity had something to do with the neglect of his work.

It is of interest to note that Higgins in these diagrams anticipated to some extent the Berzelian system of nomenclature — dephlogisticated air (D), phlogisticated air (P), inflammable air (I). He is not, however, consistent in this respect, as now and then he gives different letters to atoms of the same element so as to enable one to follow his reasoning more clearly.

Thus $S\begin{matrix}D\\d\end{matrix}$ represents an atom of the oxide of sulphur; but it is quite clear from the text that "D" and "d" are identical, the different label serving merely to enable us to follow their respective parts in the reaction under consideration.

Dalton's second assumption, which lays down similarity in weight, figure, etc., of the ultimate particles of the same substance, is likewise assumed throughout Higgins' work. This is abundantly shown by his diagrams and definitions of molecules. Some of these have been quoted already. Like the preceding proposition, it may be traced to the Newtonian root.

As regards number three, which refers to the comparative positions of atoms in fluids and solids, Higgins uses a similar idea without giving a definite verbal enunciation. Dalton does not attempt to explain how the atom "supports its dignity." Higgins assumes that the surrounding atmosphere of fire repels the neighbouring atoms.

The fourth extract, which is an enunciation of the law of the indestructibility of matter, is another fundamental conception, to which neither Dalton nor Higgins can lay a claim for originality.

Fundamentally, the work of Higgins and Dalton had the same physical basis. Undoubtedly Dalton's exposition was superior. His ideas are simple, more precise, and more clearly moulded into a unified whole. He is not so prone as his predecessor to generalize too widely, and to add speculative matter which was beyond the scope of contemporary chemistry. In this connection, it may again be emphasised that in the "New System" Dalton was enunciating an atomic theory; in the "Comparative View" Higgins was using it to combat the Phlogiston Theory. It will be remembered that he claimed that Dalton applied his theory in a general and popular way, while he used it in abstruse and difficult researches. His work would have had a better chance of survival and revitalization if he had confined himself to the popular side—as he, rather unjustly, calls it. The time was not then ripe for the elucidation of the difficult problems he set himself.

The Chemical Basis of Dalton's Theory.

The chemical basis of the Atomic Theory is, of course, the three laws of chemical combination:—(1) The Law of Constant Composition, (2) The Law of Reciprocal Proportions, (3) The Law of Multiple Proportions.

Without these fundamental truths, the atomic theory would be meaningless, and the co-ordination of all three under one fundamental concept was the real achievement of the founders of the theory. It is of interest to see how far Higgins and Dalton, respectively, were responsible for these laws.

To the first neither can lay claim. This is one of those fundamental conceptions to which philosophers, with very few exceptions, have clung. It is fairly obvious that when men thought on the composition of compounds at all, they inclined towards the view of constancy of composition. All quantitative chemistry is tacitly based on this law, and it is most unlikely that any of the early chemists had any doubts of its truth. For its actual verification we must go to the work of Wenzel, Richter, and Proust. Neither Higgins nor Dalton can lay any claim to its enunciation. Both had a keen appreciation of its implications.

The second law, too, that of interproportionality, cannot be claimed by either Dalton or Higgins. It appears first definitely in the work of Bergman, and was so largely substantiated by Wenzel that the main credit for its enunciation must go to him, and to his fellow-countryman Richter, who grasped the significance of Wenzel's work, which at the time of its first appearance did not attract much attention.

To Dalton is given the credit of the enunciation of the third law, that of Multiple Proportions; it was, in fact, widely held that it was the recognition of this law that led him to the enunciation of his theory. As Dalton is invariably credited with the enunciation of this law, the opinions of some contemporaries are worth quoting.

Daubeny, in his Introduction to the Atomic Theory (1831), referring to this law, writes:—

"It would appear that we owe to Mr. Higgins, formerly of Pembroke College in this university, the first enunciation of this latter fact, as in a work published by him in 1789, entitled 'A Comparative View of the Phlogistic and Anti-Phlogistic Theories,' he distinctly states that one ultimate particle of sulphur and one of oxygen constitute sulphurous acid, whilst one ultimate particle of sulphur and two of oxygen constitute sulphuric acid; and moreover that in compounds of azote and oxygen the ingredients are to each other in the proportion of one, to one, two, three, four, five, respectively" (p. 33).

William Hyde Wollaston, in a paper before the Royal Society (Phil. Trans., 1814, p. 5), writes:—

"The first instance in which the same body was supposed to unite with different doses of another in such proportions that one of these doses is a simple multiple of the other was noticed by Mr. Higgins, who conceived, rather than actually observed, to occur certain successive degrees of oxidation of azote, and represented the series of the combination of azote to be:—

Azote 1 with 2 Oxygen making nitrous gas;
Azote 1 with 3 Oxygen making red nitrous vapour;
Azote 1 with 4 Oxygen making yellow nitrous acid;
Azote 1 with 5 Oxygen making white nitrous acid."

Later on in the same passage Wollaston qualifies his statement by remarking that Higgins did not take great pains to ascertain the actual prevalence of the law, and that to Dalton must be given the credit for the recognition of its universal applicability. This, however, is not quite fair criticism, as when Higgins wrote, a generation previously, the science was not on a sufficiently firm quantitative basis to admit of an actual demonstration of the universal applicability of the law. That Higgins believed it to be so is evident from his work on this branch, which is dealt with later.

Wollaston, in the same passage, credits Higgins with the enunciation of Gay Lussac's Law of Gaseous Volumes, and the theory of Avogadro.

"Higgins at the same time added his opinion that such are the proportions in which these gases unite to each other by bulk (i.e., in simple numerical relation, as given above), having before observed one instance of union by exactly double bulk in the formation of water by the combination of hydrogen and oxygen, and expressed his persuasion that the number of particles in a given bulk of the different gases is the same, and that the number of particles in the compounds of azote and oxygen are successively in the proportions above stated . . .

. . . . . .

. . . . Mr. Higgins, in the instance of the union of hydrogen with oxygen, anticipated the law of bulks observed by M. Gay Lussac with respect to the union of gases, and in his conception of union by ultimate particles clearly preceded Mr. Dalton in his atomic views of chemical combination."

Similar claims to the above are made by others on Higgins' behalf. It cannot be doubted that he was the first to enunciate the Law of Multiple Proportions, but a strong claim cannot be set up for him with regard to Gay Lussac's Law of Volumes. He did recognise this law in some particular cases, notably that of water, but he does not appear to have grasped its complete significance. It would have been almost impossible at the time he wrote, twenty-one years before Gay Lussac's Memoir "on the combination of gaseous substances with one another," to collect sufficient evidence to demonstrate the law beyond doubt.

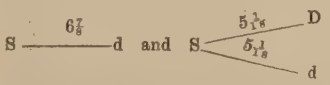
His claim to Avogadro's hypothesis cannot be substantiated. He certainly states it in one particular case, that of hydrogen and oxygen, but from other portions of his work it is clear that he in no way regarded it as a general rule.

The Law of Multiple Proportions.

Higgins' first exposition of this law occurs in the chapter on the vitriolic acid. In the early pages of this chapter he examines closely the prevailing phlogistic doctrine that sulphur is not a simple substance, but a compound of a certain basis and phlogiston. After reviewing the evidence, for and against, at some length, and after examining the quantitative composition of sulphur dioxide and sulphuric acid as given by the best chemists of the time, he concludes "that the ultimate particles of sulphur and oxygen contain equal quantities of solid matter, for oxygen suffers no considerable contraction by uniting to sulphur in the proportion merely necessary for the formation of volatile vitriolic acid. Hence we may conclude that in volatile vitriolic acid a single ultimate particle of sulphur is intimately united only to a single ultimate particle of oxygen, and that in the perfect vitriolic acid every single particle of sulphur is united to two of oxygen, being the quantity necessary to saturation."[3]

Here we have the law of multiple proportions clearly recognised for the compounds of sulphur with oxygen. In this instance and in others he is led astray by the prevailing Lavoisierian doctrine of oxygen as the principle of acidity, and the non-recognition of hydrogen as a constituent of all acids. That he is wrong, according to modern ideas, in the composition of the substances does not invalidate his reasoning. An examination of Dalton's table of symbols discloses similar misconceptions.

Higgins' representations of these molecules are



It will be noticed that he considers the forces binding sulphur and oxygen to

[3] For facility in reading, "dephlogisticated air" has been altered to "oxygen" and "inflammable air" to "hydrogen" in quotations from Higgins' earlier book. No change has been made which would in any way alter or enlarge on the writer's meaning.

be greater in the diatomic than in the triatomic molecule. The use of the capital and small letters for the atoms of oxygen serves merely to indicate individual atoms of the substance.

He also uses his conceptions to determine the relative weights of the atoms of sulphur and oxygen, which Dalton claimed to be a novelty in his theory. His assumption that the atoms of sulphur and oxygen were of equal weight is quite defensible on his assumption that sulphur dioxide consisted of one atom of sulphur and one of oxygen.

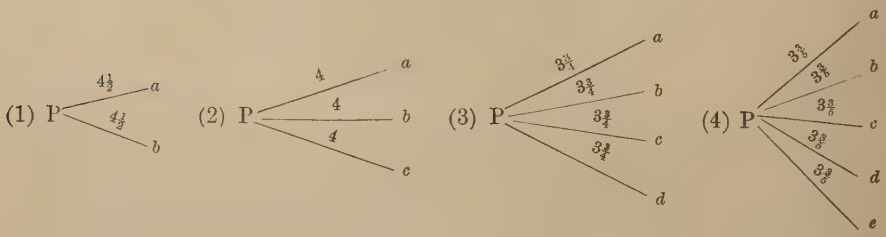
In the succeeding passage he gives us the Daltonian conception of water, and approaches very closely the later work of Gay Lussac and Avogadro. This is one of the passages that led to the claims made for him by Wollaston and others quoted earlier :—

"As two cubic inches of hydrogen require but one of oxygen to condense them, we must suppose that they contain equal numbers of divisions, and that the difference of their specific gravities depends chiefly on the size of their ultimate particles, or we must suppose that the ultimate particles of hydrogen require two or three or more of oxygen to saturate them. If this latter were the case, we might produce water in an intermediate state as well as the vitriolic or nitrous acid, which appears to be impossible; for in whatever proportion we mix our airs, or under whatsoever circumstances we combine them, the result is invariably the same. This likewise may be observed with respect to the decomposition of water. Hence we may justly infer that water is composed of molecules formed by the union of a single particle of oxygen to a single ultimate particle of hydrogen, and that they are incapable of uniting to a third particle of their constituent principles."

In addition to applying these views to the compounds of sulphur and oxygen and to water, he also applies it to the compounds of nitrogen and oxygen in the following passages. In these he also attempts to define the forces holding the various atoms in combination.

After examining the quantitative relations of Nitrous Air, he expresses himself as of the opinion that every primary particle of nitrogen is united to two of oxygen, and that these molecules are surrounded by a common atmosphere of fire.

He then assigns the formulae



to the oxides and acids of nitrogen. The presence of hydrogen in all acids had not then been recognised. The attractive forces between nitrogen and oxygen calculated from his figures for affinity range from $4\frac{1}{2}$, in the triatomic molecule, to $3\frac{3}{5}$ in the hexatomic one. He concludes that at the latter stage in the colourless nitrous acid "no more oxygen can unite to the nitrogen as having its whole force of attraction expended on the particles of oxygen *a, b, c, d, e.* This illustrates the nature of saturation."

The last portion of this extract is interesting as a hint of later speculations on valence. Sufficient has been given to show that, by the evidence of his own writings and the judgment of his contemporaries, Higgins was the first to enunciate the Law of Multiple Proportions, the Keystone to the Atomic Theory. Dalton's enunciation was undoubtedly independent, but nearly twenty years later.

It is obvious, then, that as far as the chemical basis of the theory was concerned, Higgins' ground-work was as secure as Dalton's. Both similarly grasped the full significance of the laws of proportion, and used them to build up atomic theories whose details are almost exactly alike. We shall now see how the theory was applied by the two.

Some Applications of the Theory.

The most interesting feature of Dalton's work, and the one on which he laid particular stress, was its application to the relative weights of atoms, both of simple and compound bodies, and to the number of atoms in the various compounds. This was beyond doubt the most fruitful line of expansion, and was the means of laying the present exact quantitative basis of the science. In these lines Dalton's work is distinctly superior to Higgins'. He extended his generalisations, and compiled tables of relative weights. These, of course, were very inaccurate. They could not be otherwise, but they were a very significant advance on earlier work.

It must not be thought that Higgins neglected entirely this side of the work. In his book he gives instances of how these weights may be deduced, but he does not systematically compile a table.

For example, since he regards sulphur dioxide as one atom of oxygen combined with one atom of sulphur, taking into account the composition by weight, he says that the ultimate particles of sulphur and oxygen are of equal weights ("Comp. View," p. 36). This is in many ways a shrewder deduction than Dalton's table, which gives sulphur as 13 and oxygen as 7, and expresses more accurately the quantitative composition of the gas.

In other similar applications we see that Dalton is much readier to apply his principles and to give his results in the form of tables, while Higgins' must be gleaned throughout his book.

This is Dalton's real claim to the theory. Higgins certainly anticipated him in the principle and in many of the details, but Dalton excelled in the application of the theory. He turned the current of thought into the profitable

channels of chemical constitution, while Higgins attempted to explain the nature of chemical action—an attempt praiseworthy, no doubt, but still beyond the scope of the time. His line of extension of the atomic frontier, handicapped as it was by his plausible and ingenious but still untenable theory of affinity, was not at all as profitable as Dalton's.

It should not be thought, of course, that Dalton's theory led to an immediate clarification of chemical constitution. Many of his rules were, as one would expect, very erroneous. Many false notions had to be eradicated, and much of his work supplemented, before any lasting effects could be seen.

Even Dalton himself did not seem to quite appreciate some of the implications of his theory. He rejected the law of volumes of Gay Lussac, despite the overwhelming experimental evidence and its close relation to his own theory, a fact all the more surprising as he himself seemed, in earlier work, to have recognised this law. Indeed, some historians have gone so far as to call it the Dalton—Gay Lussac law; but, whatever Dalton's earlier views were, in the second part of his "New System" he speaks of Gay Lussac's conclusions as erroneous. This fact makes Higgins' recognition of the Volume Law very significant.

The principles had been laid down too strongly by Dalton to be entirely abandoned, and, after years of chaos and uncertainty, when it often seemed likely that the theory would fall, the inconsistencies were cleared up, and the work of Gay Lussac, Avogadro, Berzelius, and many others made it possible for the theory to reach its present state.

Higgins' work did not get such a chance. Though, fundamentally, the Daltonian hypothesis is the one Higgins used twenty years previously, his work was not followed up, and the later advances were postponed till Dalton's time. Those are, in brief, the essentials of Higgins' claim. Physically and chemically his principle anticipated Dalton's. His tenets are the same, and his recognition of the law of multiple proportions, which is the most important constitutional implication of the atomic hypothesis, sets a seal on his work.

Some Contemporary Opinions.

That Higgins' claim to priority has not been over-stated is clear from contemporary opinions.

William Hyde Wollaston, in the paper which has been quoted earlier, says that Higgins, "in his conception of union by ultimate particles, clearly preceded Mr. Dalton in his atomic views of chemistry" (Phil. Trans., 1814, p. 5).

Humphry Davy, writing in 1811 of the "Comparative View," says: "In this elaborate and ingenious performance Mr. Higgins has developed many happy sketches of the manner in which (on the corpuscular hypothesis) the particles or molecules of bodies may be conceived to combine; and some of his views, though formed at this early period of investigation, appear to me to be more defensible, assuming his data, than any which have been since advanced" (Phil. Trans., 1811, p. 15). He then quotes some examples. Higgins' prior

claim to the theory is also expressed by him in his "Elements of Chemical Philosophy," p. 107.

Daubeny makes the point very clearly in his comment:—

"It is a pity for Mr. Higgins' reputation that he had not struck out this idea a few years later, when, as its correctness could have been substantiated by an appeal to facts, it is possible that his genius might have overleaped the boundary that separates the point to which we are led by his researches from that afterwards attained by Mr. Dalton" ("Introduction to the Atomic Theory," p. 33).

One other passage is worth quotation and comment. It is probably the source of most of the erroneous historical references to Higgins' work. It is from the pen of Thomas Thomson, the author of the "System of Chemistry" and the "History of Chemistry," which were standard works in the first two decades of the last century. The authors' comments are in parentheses:—

"The work of Higgins on phlogiston is certainly possessed of much merit; and he anticipated some of the most striking subsequent discoveries. But when he wrote metallic oxides were so little known and so few exact analyses existed that it was not possible to be acquainted with the grand fact that oxygen, etc., always unite in determinate proportions which are multiples of the minimum proportions." (Almost every page of Higgins' work, as has been shown already, makes the inaccuracy of this clear.)

"The Atomic theory was taught by Bergman, Cullen, Black, etc., just as far as it was by Higgins." (This is obviously ridiculous, as an examination of these writers' work shows.) "The latter indeed states some striking facts respecting the gases, and anticipated Gay Lussac's Law of Volumes; but Mr. Dalton first generalised the doctrine and thought of determining the relative weights of atoms of bodies. He shewed me his table of symbols, and the weight of the atoms of 6 or 8 bodies in 1804, and I believe the same year explained the subject in London, in a course of lectures delivered in the Royal Institute. The subject could hardly have been broached sooner. But about the same time several other persons had been struck with the numbers in my table of metallic oxides published in my chemistry, and the doctrine would certainly have been started by others if Dalton had missed it."

This is the most unfavourable reference to Higgins' work we have met with in contemporary literature. It is not very correct, and Thomson appears to be at pains to point out the merits of his own work, and is very sparing with his praise to both Higgins and Dalton.

Conclusion.

It is not hard to understand why Higgins' work was neglected. It was written to deal with the phlogiston controversy, and, as that theory collapsed shortly afterwards, the immediate interest of the book was destroyed. Also the views it contains were too far ahead of chemical thought at the time.

As Daubeny says, it would be better if they had come ten or fifteen years later. The prime need of chemistry when Higgins wrote was, not the development of an atomic theory, but the sweeping away of the phlogiston theory. Until that had been done, the basis of the science was not secure. Higgins' early acceptance of the anti-phlogistic doctrine, and his dissemination of it, are worthy of the highest praise. Davy says he was the first in England to advocate this doctrine, and Kirwan, who was for long an uncompromising opponent of the chemistry of Lavoisier, was won over by the exposition of his younger countryman. If Higgins' work contained nothing else but his advocacy of the anti-phlogiston doctrine, it would still be worthy of the highest praise.

It is unnecessary to dwell on the mistakes in his work. They are no more than will be found in any other writer of the time. Many of them, such as his idea of the composition of water, he shares with Dalton.

A criticism of his work which is very common in the few text-books that mention his name is that he was a speculator rather than an experimentalist, and that, by not following up his work on the atomic theory, he proved his want of faith in it. Undoubtedly Higgins was a speculator, but, nevertheless, he speculated on facts as they were reported to him by the best chemists of his time, and on the results of his own experimental work, which he quotes largely throughout his book. In this he sets the precedent for Dalton, who, according to Roscoe and Harding, "derived all the numbers in his earlier table from analyses, by chemists of reputation, and generally accepted by the chemists of the time; not one of them appears to be due to Dalton himself" ("A New View of Dalton's Atomic Theory," p. 30). Later on we read that Dalton never had any great skill in analysis.

All the evidence goes to show that Dalton's work was very brilliant speculation, by which he so comprehended the basis of chemical relations that it has stood the test of time to the present day. It is most illogical, then, to condemn Higgins as a mere speculator, more particularly when it might be seen from his work that experiment was one of his main cares, and that the very same objections which have been put forward against him might, with equal or even greater validity, be made against Dalton.

The fact that Higgins did not follow up his work immediately does not mean that he did not appreciate its significance, but that others did not. Much important work has been left unnoticed for even longer periods. After his book was published Higgins does not appear to have been over-prosperous, and circumstances after his return to Dublin a few years afterwards, in 1791, turned his attention in the direction of applied chemistry, which in his later days he seems to have regarded as of paramount importance. If he had received the encouragement that Dalton did, his work would undoubtedly have formed the basis of atomic chemistry.

Nothing he has done can detract from the glory that is the rightful meed of Dalton, who must be regarded as the father of the modern theory, since it was his work that was the main-spring and inspiration of later events. But,

nevertheless, Dalton was not the first, and, but for an accident of circumstances, the theory of Dalton might easily be the theory of Higgins.

Higgins in one of his books expresses the belief that Time, the parent of truth, will operate in his favour. He was sadly mistaken. Time has done nothing to concede to him that meed of praise which was his due. His influence, as speculator, experimenter, applied chemist, and teacher, on the science which was the main interest of his life deserves much more than the scanty notice it has been accorded.

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No. 16.

THE INTEGRATION OF LIGHT BY PHOTO-ELECTROLYSIS.

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AND
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[Read December 18, 1928. Published separately January 29, 1929.]

Introduction.

During its life the green plant acts as an integrating mechanism for light energy, since it carries on photosynthesis, the products of which can be measured with some degree of exactitude. There are, however, obvious drawbacks to using the living plant as an integrator. Moreover, as the rate of photosynthesis may be limited by factors other than the intensity of illumination, the result so obtained would generally be erroneous.

Since the electric current passing through a photo-electric cell is directly proportional to the light falling on it, we can evidently integrate the latter over any period of time by measuring electrolytically the total quantity of electricity that has passed, provided that a sufficiently delicate and reliable voltameter is available. Two such electrolytic methods are described below.

The problem has been rendered much simpler by the advent of the Burt vacuum sodium cell, which apparently combines the reliability of the vacuum cell with a sensitivity which we have hitherto only found in the more variable gas-filled cells. In the Burt cell the metallic sodium is deposited on the inner surface of an evacuated glass bulb by electrolysis of the glass. The cell resembles an electric lamp with rather more than half the inner surface of the bulb "silvered" with metallic sodium. These cells are made with either end-on or side apertures; those of the latter type are the more sensitive, since the sodium surface is larger and better illuminated.

We had previously worked with sodium and potassium vacuum cells, the colour-sensitivities of which are shown in another paper (1928). It may suffice to say that the maximum of the sodium cell is in the near ultra-violet, whereas that of the potassium cell is in the violet. Cells, even of the same metal, may differ slightly in colour-sensitiveness, but there is no reason to think that the colour-sensitiveness of the Burt cell differs very appreciably from that of other sodium cells.

As previously described, a potassium vacuum cell, designated *H*, was standardised and found to give 10^{-9} ampere when illuminated with 40 metre

candles, with anode potential 60 volts, the open carbon arc being the source. This cell was mounted on the under side of the ebonite lid of a light-tight box, the pupil of the cell occupying a hole in the lid 1·4 cm. in diameter, covered by a window of double surface flashed white opal glass, cemented to the outside of the lid. This we found to be the most suitable diffusing agent. It, however, reduces the reading given by the light from a uniformly grey sky by about one-half.

The sensitiveness of this cell was about four times as great as that of a similar, but smaller, cell which we had used as a standard for several years previously. These vacuum cells remain constant in sensitivity—at least, over an interval of about eight months no change could be detected when illuminated with a test lamp at constant voltage, the lamp being reserved exclusively for this purpose.

The Burt cell is very conveniently mounted in a radio-valve socket. In order to make full use of its large receiving surface and of oblique light, it was put in position immediately below a sheet of the opal-flashed glass, 26·5 × 21·5 cm., which constituted the lid of the box. High-tension ignition cable was used as leads.

Comparing two Burt cells with our standard (*H*) in daylight with 60 volts anode potential, we found the following sensitivities:—Burt No. 188, 19·4 times as sensitive as *H*, viz., 2·06 metre candles per 10^{-9} amp.; No. 223, 50·3 times as sensitive as *H*, viz., 0·795 m.c. per 10^{-9} amp. From data supplied by Dr. Burt it was calculated that B. 224 had 92 per cent. of the sensitivity of B. 223, viz., 0·865 m.c. per 10^{-9} amp., at 60 volts, or 1·15 microamperes per 1,000 m.c.

Merely as a matter of convenience, cell B. 224 was used in all the following experiments.

The Photo-electrolytic Production of Alkali.

The photometer was placed on a table, near a window facing north, sloping at about 30° to the horizontal. The negative lead was connected with a 10,000 ohm safety resistance, the other end of which was connected to the negative of a 60 volt dry battery. The positive lead of the photometer was connected by the usual mercury tube with a platinum electrode, which dipped into an electrode vessel of resistance glass, such as used in hydrogen ion concentration measurements, having a side tube like an inverted U dipping into a small beaker. The other electrode was placed in the beaker and connected with the positive terminal of the battery.

The electrode vessel and beaker were filled with the following solution:—to distilled water was added the indicator brom-thymol blue, 0·04 per cent., in the proportion of one drop per c.c. of water. The resulting yellow colour showed that the water was at least as acid as *pH* 6 owing to the presence of dissolved carbon dioxide. A minute amount of solid sodium bicarbonate was added, so that the solution turned greenish. It was then found to be at *pH* 6·5. On pouring the solution into the vessel and beaker and making connection, the

photo-electric current causes the production of alkalinity at the kathode, so that, on a bright November day at one o'clock, the development of a blue colour, denoting *pH* 7·2 or over, could be seen close to the electrode within a few minutes; or, watching carefully, the change could be noted within 35 seconds. Next, on a November afternoon at 3 p.m., the photometer was moved to a south window; the sun was shining through white clouds. The electrode used happened to be gold, merely for convenience in size, and it was bent into a J shape. Using a lens, the sky could be viewed through the bend of the J. The initial *pH* was 6·8, but within ten seconds after making connection a narrow coating of blue could be seen round the electrode. It is of interest to consider the magnitude of the chemical changes involved; assuming the illumination incident on the photometer to have been 20,000 m.c., the current would have been 23 microamperes; taking the electro-chemical equivalent of sodium as 238×10^{-6} g., 238×10^{-3} mg. would be deposited per microampere in 10 seconds. This gives 55×10^{-6} mg. of sodium, or $2{\cdot}4 \times 10^{-6}$ mg. of hydrogen for the visible effect noted above. Assuming that the volume of the layer in which the blue colour was produced was 0·1 c.c., in pure water the colour change would only involve a diminution in the hydrogen ion content of $0{\cdot}0095 \times 10^{-6}$ mg., which is about 250 times less than the change involved in the experiment. Thus, by boiling out most of the carbon dioxide, and adding an even more minute amount of bicarbonate than was actually used, it would be possible considerably to increase the sensitiveness of the reaction.

On allowing the current to continue, the contents of the kathode vessel became blue, and the liquid round the anode in the beaker became yellowish. There is no reason why this should not be made a quantitative reaction by titrating with a microburette and very dilute acid or alkali, so as to restore the hydrogen ion concentration to its original value. For this purpose the normality of the bicarbonate solution must be known. Also it is advisable to have a stop-cock in the connecting-piece, as the liquid is apt to syphon over if the apparatus be disturbed.

For the integration of light over a more prolonged period, one or more days, special precautions would have to be taken to prevent the invasion of carbon dioxide from the air, though not till *pH* 8 is reached is the partial pressure of the gas in the bicarbonate solution reduced below that normally present in the air.

The Photo-electric Deposition of Copper.

An alternative method, the electro-deposition of copper, was next tried. Using two platinum electrodes, dipping into a beaker containing 10 c.c. of copper sulphate, of concentration 1 mg. Cu per c.c., the photometer in the south window was connected at 5 p.m. on November 23, and disconnected at 1 p.m. on November 29. The under surface of the kathode had a visible deposit of copper. This was dissolved in warm dilute sulphuric acid, neutralised with solid sodium bicarbonate, and estimated roughly, colorimetrically, as described later; the amount found was about 0·5 or 0·6 mg., i.e., about 0·1 mg. per day.

Some of the deposit had probably been re-dissolved, since the electrodes were fairly close together, and the solution, originally at *pH* 4·6 or over, viz., less acid, had increased in acidity to *pH* 3·8, as shown by brom phenol blue. This re-solution error may be avoided by proper spacing of the electrodes, and by using the inverted U connecting-piece. The effect of using a copper wire as the anode was, however, tried, and the exposure lasted from 5 p.m. on November 29 till 11 a.m. on December 3, over three days, of which November 30 was very dull, December 1 sunny, and December 2 an average day. The platinum electrode was visibly dimmed on the upper surface, and about 0·3 mg. Cu was estimated. That no copper was re-dissolved from the anode in this experiment is shown by the fact that the solution had not become more acid. This method of avoiding re-solution is extremely convenient. There is probably less potential difference between the voltameter terminals with the copper than with the platinum anode, as the platinum kathode must soon become coated with a thin layer of copper. In any case this potential difference would be less than a volt. As the current through the photo-electric cell is but little affected by so small a variation in its working pressure, which is not less than 60 volts, the effect may be neglected.

It remains to consider what amount of copper one might expect to be deposited in a normal winter day. On November 30 observations made at sea, with an apparatus previously described (Poole, 1925; Poole and Atkins, 1925, 1928), gave, between noon and 3 p.m., a mean vertical illumination of about 7,200 metre candles. The day was very dull throughout. As an approximation one may reasonably take 5,000 m.c. as the average for such a ten-hour day. November 9 was a clear sunny day, somewhat comparable to December 1. The illumination rose as high as 36,000 m.c., and a mean of 15,000 m.c. for the ten hours seems quite a possible figure. December 2 may be taken as in between, say, 10,000 m.c. Three such days would give 10,000 m.c. as an average ten-hour value. Since copper is deposited at the rate of 0·3292 mg. per ampere per second, or 1·135 g. per hour, a cell such as B. 224, in which 865 m.c. produce one microampere—or 1·15 μa. per 1,000 m.c.—would deposit $1.135 \times 1.15 \times 10^{-6} \times 10 \times 10$, i.e., 0·131, mg. of copper in 10 hours at 10,000 m.c. A summer day, with a possible maximum of over 150,000 m.c. on the photo-electric scale, may be taken as averaging 50,000 m.c. for 14 hours. This would deposit 0·917 mg. of copper.

Method of Estimating the Copper Deposited.

The estimation of the copper is carried out according to the potassium ethyl xanthate method of Scott and Derby (1922), which was subjected to a critical examination by Supplee and Bellis (1922). A stock solution of copper sulphate (cryst.) is made up to contain 3·9283 g. per litre. Of this 1 c.c. contains 1 mg. of copper. On diluting 10 c.c. of this to a litre, the standard containing 0·01 mg. of copper per c.c. is obtained. The concentration of the unknown copper solution is estimated colorimetrically by comparison against

suitable proportions of the standard, each being made up to 100 c.c. and viewed in cylinders of clear glass (Nessler tubes). To each a solution of potassium ethyl xanthate, 1 g. per litre, is added; this solution should be stored in the dark, and is more sensitive if made up fairly frequently. Supplee and Bellis recommend the addition of 10 c.c. of xanthate to each 100 c.c. (or 90 c.c.) of copper solution, but for very minute amounts we find that a smaller volume, 2 c.c., suffices. This is of value when comparing solutions of closely similar colour, since a smaller blank reading is given with the reagent and water distilled from glass or from a good tin-worm copper still. For this final comparison it is convenient to compare the unknown, standing at the 100 mark level in a tube, with a standard slightly stronger; from the latter liquid is removed in successive small quantities till a balance is obtained. Hehner tubes, which are graduated and have a stop-cock near the bottom, are convenient for this purpose. We have been able to distinguish between solutions differing in copper content by as little as 0·002 mg. in 100 c.c. It is obvious that this delicacy suffices for the estimation of the daily copper deposit with fair accuracy, even in extremely dull weather. Were an amplifier giving constant amplification to be produced, it would be possible to use less sensitive chemical reactions; but as it is, the methods are equal to the occasion.

Method Suggested for Routine Integration of Daylight.

It is, of course, necessary that the photometer should be exposed horizontally to the whole sky. In making observations throughout the day, using the apparatus previously described, it was our custom to mount the photometer on the flat roof of the Marine Biological Laboratory at Plymouth. In this case the photometer, containing an ordinary potassium vacuum cell, was a gun-metal box used for obtaining submarine illuminations. Its heavy high-tension ignition cable leads were brought down to the laboratory, where the potentiometer outfit was conveniently placed. There is no reason why the Burt cell should not be mounted similarly in a water-tight vessel, heavy enough to avoid being blown over; but provisionally we propose using the present photometer, covered with a large bell-jar. It would appear advisable to have the high-tension battery in the laboratory rather than on the roof, for the sake of minimising leakage. In order to maintain a more constant voltage, it is also proposed to use accumulators rather than a dry battery.

We wish to acknowledge our indebtedness and to express our thanks as follows:—to the Government Grant Committee of the Royal Society for making possible the purchase of the Burt cells; to the Royal Dublin Society for the use of apparatus and for laboratory facilities connected with the standardisation of the cells; to the Marine Biological Association of the United Kingdom for general laboratory facilities and apparatus.

SUMMARY.

It is possible to use a vacuum photo-electric cell for the integration of light. A Burt sodium cell gave 1·15 microamperes per 1,000 metre candles. On a bright November afternoon it was possible to detect the production of alkali in a dilute bicarbonate solution within 10 seconds.

The current may also be used for the deposition of copper, about 0·1 mg. per day being deposited with photometer sloped in a south window. An average winter day should give about 0·13 mg., with photometer in the open, placed horizontally; in summer nearly 1 mg. might be expected.

The potassium ethyl xanthate method enables one to distinguish between solutions differing in copper content by 0·002 mg. per 100 c.c.

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No. 17.

A NOTE ON GAS ANALYSIS.

By JAMES T. DONNELLY, C. HAMILTON FOOTT,
AND
J. REILLY.

[Read December 18, 1928. Published separately January 29, 1929.]

During the last three years some hundreds of accurate gas analyses were carried out in this laboratory in connection with research work on the distillation of pre-oxidised fuels (J. Soc. Chem. Ind., 1928, **47**, 54 T, etc.). Since 1926 these analyses were made on a Bone and Wheeler apparatus (J. Soc. Chem. Ind., 1908, **27**, 10), obtained from a grant given by the Royal Dublin Society. During the course of this work a number of modifications have been introduced, and it has been suggested that a short note on the improved apparatus and its erection would be of value to subsequent workers.

The apparatus is mounted in the centre of the laboratory on a specially constructed bench, twenty-four inches high. This height is suggested as most convenient for the average worker. The bench is divided by an eighteen-inch partition, on one side of which are mounted a nine-by-eighteen-inch sink and three taps connected direct to the high pressure water main, and on the other the apparatus. Two of these taps are used for the water pressure supply and the suction pump for the apparatus, and the third for general purposes. An idea of the apparatus as fitted up can be gathered from the photograph, fig. 1, while the various connections and arrangements of stop-cocks may be understood better from the diagrammatic sketch, fig. 2.

In the standard form of apparatus, as supplied, the gas sample to be analysed is collected in a test tube, and is introduced by inverting the tube under a bell in a trough of mercury, whence it is transferred to one side of a graduated U-tube (the gas measuring burette), expanded to a predetermined volume, and the pressure read. The gas is then brought into contact with various reagents introduced into the bell. The pressure is again read at the constant volume after the removal of each constituent, the differences in the pressures representing proportionately the volumes of the constituents removed.

The gas was manipulated by raising and lowering a mercury reservoir with the aid of a pulley and ratchet. The method now more generally in use is to employ the direct pressure of the water main and the suction from a water

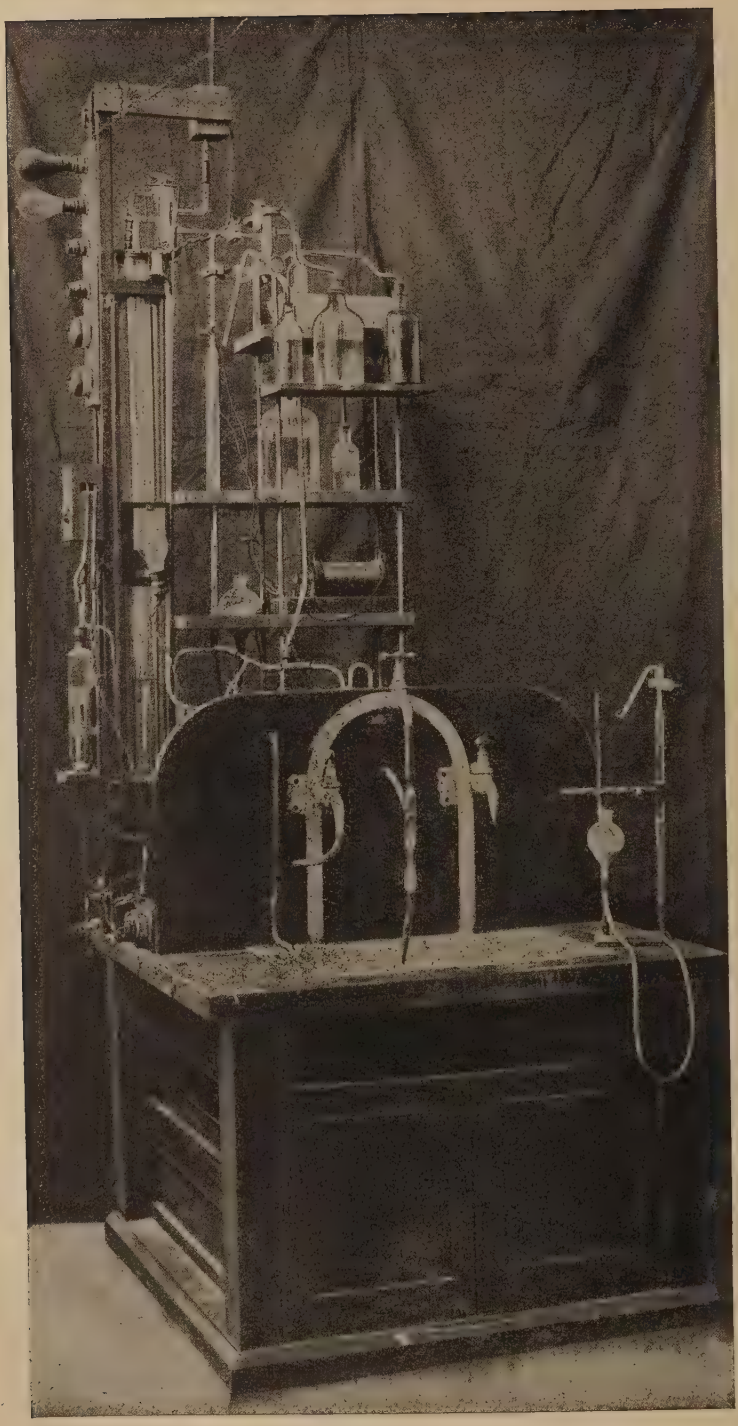


FIG. 1.

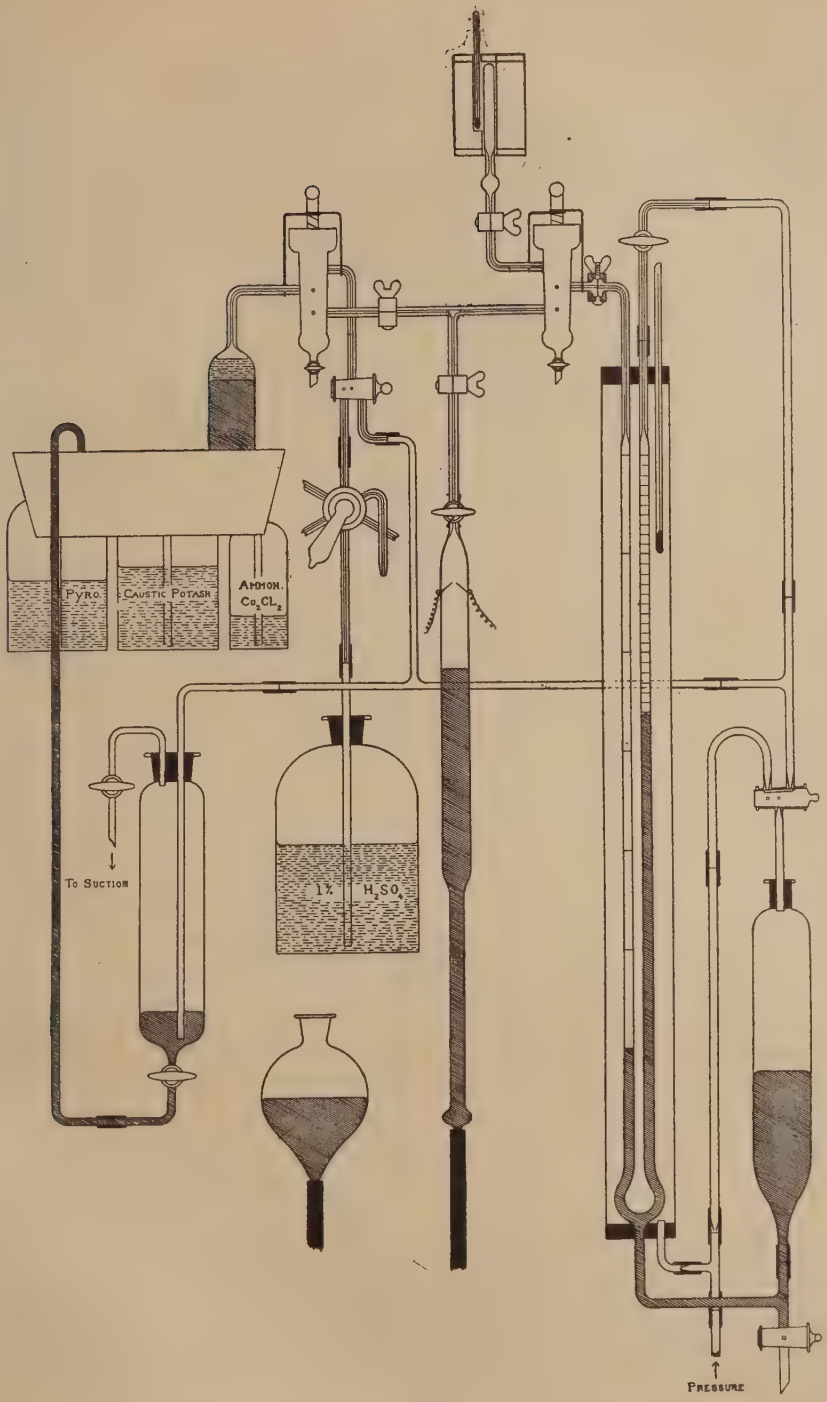
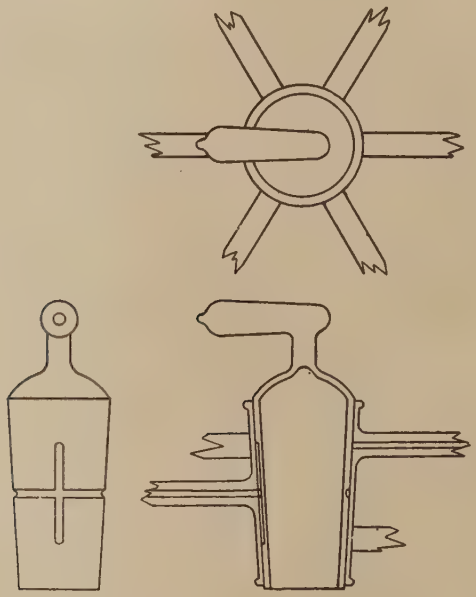

Pyro.
Caustic Potash
Ammon. Co_2Cl_2
To Suction
1% H_2SO_4
Pressure

Fig. 2.

suction pump to raise and lower the mercury. The mercury reservoir is clamped so that the level of the mercury is near the bend of the U-tube, or a little above it if the pressure of the water is insufficient to force the mercury over into the bell from the lower level. The top of the reservoir is closed by a two-way stop-cock, one side of which is connected direct to the water main, and the other, through a mercury trap, to the suction pump. Small tapered file nicks in the sides of the holes in the plug of the stop-cock facilitate the fine adjustment of the mercury level in the gas measuring burette. When the stop-cock is in the "off" position, a groove in the plug connects the water main to the suction pump, which reduces the pressure and provides a stream of water for washing the mercury in the trap. A drain-cock, included at the lowest point between the mercury reservoir and the gas measuring burette, enables the system to be easily emptied of mercury.



SIX-WAY TAP

FIG. 3.

A frequent cause of breakage lies in allowing the mercury when under vacuum to ascend the gas burette too quickly, thus fracturing the ends of the tube. This has been overcome in our modification by introducing a restriction of about one millimetre diameter in the form of a jet between the water main and the mercury reservoir. To prevent "whistling," the jet should be pointed in the opposite direction to that in which the water is flowing. Between this

jet and the main a T-piece is inserted to supply water to the cooling jacket around the gas burette, and a constriction included to control the rate of flow.

Flanged joints should be inserted in the apparatus where necessary to permit of the easy removal of parts for repairs, and should include one between the gas measuring burette and the stop-cock adjoining it. After trying various preparations, the best sealing material for these joints was found to be gold size.

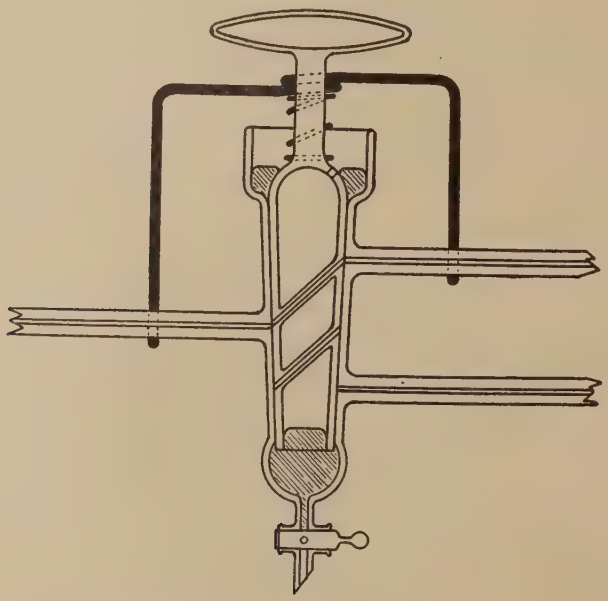
The collection in test tubes over mercury of gas for analysis is a method which necessitates the direct handling of the metal. Except where a number of samples of gas are required to be kept for some time, direct contact of the mercury with the skin may be avoided by using the specially devised gas sampler shown at the side in fig. 1. To take a sample with this device, the short arm of the two-way stop-cock is connected to the apparatus containing the gas by a short length of rubber pressure tubing, and the air in the connecting tube removed by using the gas sampler as a pump. The sample is then withdrawn and introduced into the apparatus directly by inserting the long arm of the sampler under the bell.

The older method of introducing reagents is to insert a pipette containing the liquid under the edge of the bell. A more convenient way is to employ the head of mercury in the bell to suck the reagents from bottles connected to the apparatus as required. By the use of the six-way tap, shown in fig. 3, the bottles containing the solutions of pyrogallol, potassium hydroxide, ammoniacal cuprous chloride, and 1 per cent. sulphuric acid are connected to the apparatus, and unnecessary handling of the reagents avoided. The fifth arm of the tap is left blank for the introduction of any special reagent not in frequent use, whilst the sixth is connected to the two-way stop-cock leading to the bell. The tap is so constructed that by rotating the plug the sixth arm may be connected in turn to each of the other five. The six arms are placed equidistantly around the barrel in three planes, two in the lower, three in the upper, and the sixth arm in the middle. No holes are drilled through the plug of the tap, but a ringed groove is cut opposite the centre arm. A second longitudinal groove, intersecting the central ring at right angles, is also cut long enough to connect the outer arms with the centre. This longitudinal groove is cut immediately below a mark on the handle, so that the position of the plug may be easily seen.

A two-way stop-cock connects the bell alternatively to the sixth arm of the reagent tap or to the suction pump through the mercury trap. The reagents introduced into the bell through the former may be removed by the suction, and any mercury which is drawn over at the same time is collected and washed in the trap. The right-hand limb of the gas measuring burette is also connected to the mercury trap through the stop-cock at the top. A tube leading from the bottom of the mercury trap to the trough under the bell enables clean mercury to be forced back to the trough by shutting the stop-cock to the suction pump.

Leakage at the stop-cocks is a frequent source of error in an apparatus of this type after it has been in use for some time, especially if the gas is kept at

greatly increased or reduced pressures during analysis. The possibility of leakage can be minimised by using wide-diameter mercury-sealed stop-cocks. The stop-cock shown in fig. 4, which has been found to be extremely satisfactory, has a hollow plug, three-quarters of an inch in diameter, at the centre, and can be sealed with mercury at the top and bottom. A hole drilled at the top of the plug allows mercury to run down the hollow centre into the well to seal the lower join, and a cup round the top of the stop-cock retains sufficient mercury to seal the upper join. When the plug is removed for greasing, the mercury collects in the well, and can be run off through the drain-cock provided for that purpose.



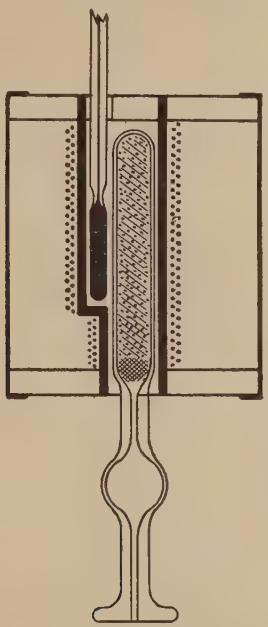
MERCURY SEALED STOPCOCK

FIG. 4.

These large sealed stop-cocks are only recommended for the two stop-cocks situated between the bell and the gas measuring burette, which are continually in use, and where the gas undergoing analysis is subjected to big variations in pressure. Spring clips of the type shown in fig. 4 are an advantage on all the stop-cocks to keep the plugs in position. A suitable grease for the taps consists of about equal parts beeswax and vaseline, the proportions being varied according to the average temperature of the room in which the apparatus is situated.

The method of using of copper oxide for estimating hydrogen in the presence of hydrocarbons was first applied by Jäger (Jl. f. Gasbeleuchtung, 1898, **41**, 764). Since then several workers have described apparatus applying this principle to

gas analysis, notably King (Fuel, 1922, i, p. 103). The apparatus described below, fig. 5, was constructed by the authors, and has been in use for some time. It consists of a silica tube, 6 cm. long by 1 cm. in diameter, closed at one end, and lightly filled with a mixture of equal parts of short fibre asbestos and fine copper oxide. The other end is drawn off, expanded to a bulb, and connected in a vertical position above the apparatus to the two-way stop-cock at the top of the gas burette by a flange joint. A small electric furnace, wound so that the full pressure of the electric main gives a temperature of 600° C., is placed



COPPER OXIDE FURNACE FOR HYDROGEN ESTIMATION

FIG. 5.

around the silica tube. A switch is arranged to give an alternative circuit through a lamp of a resistance chosen to give a maximum furnace temperature of 270°. One advantage of having alternate circuits is that by using the full current the furnace may be quickly heated to the desired temperature of 280° before switching in the resistance.

When the analysis has reached the stage where the hydrogen is to be estimated, the sample is stored in the explosion chamber, while the copper oxide tube, which has already been heated to 280°, is evacuated. The gas measuring burette is employed as a pump to expel the air from the oxide tube into the

adjacent bell. The evacuation is usually complete after five or six "strokes." The sample is then removed from the explosion chamber to the gas burette, and allowed to slowly enter the copper oxide tube. With the furnace in a vertical position, the bulb adjoining the copper oxide tube prevents droplets of moisture or mercury, which may have become trapped in the capillary tubing, from being carried into the hot oxide tube, and also enables the water formed by the combustion to be removed. As the copper oxide tube is large enough to contain the whole of the gas sample, combustion of the hydrogen is complete in a very short time, after which the copper oxide tube is again evacuated and the contraction in the volume of the gas sample measured. On completion of the analysis, the copper oxide tube is filled with oxygen, and the temperature of the furnace raised to 600° to reoxidise the copper. A pocket in the electric furnace allows a thermometer to be inserted alongside the copper oxide tube, so that the temperature may be watched during the combustion of the hydrogen.

It is well recognised that with the constant handling of mercury there is a definite risk of poisoning, and so one feature to which particular attention was paid in the reconstruction of this apparatus was the elimination, where possible, of the necessity of handling mercury, and the avoidance of methods which tended to splash the metal about the tray of the apparatus and over the floor of the laboratory. Another precaution taken was that all shelves on the apparatus on which mercury was used were beaded and provided with small plugged holes, so that spilled mercury could be collected and drawn off. Also, the concrete floor of the laboratory was resurfaced with a composition which gave a smooth finish, easy to keep clean, and on which the mercury did not collect in small crevices or tend to scatter in very fine particles.

The six-way tap, shown in fig. 3, and the wide-diameter mercury sealed stop-cock, shown in fig. 4, were made to our design by the Scientific Glass-Blowing Co., 12 Wright Street, Manchester.

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University College, Cork.

No. 18.

THE PHOTO-ELECTRIC MEASUREMENT OF THE ILLUMINATION IN BUILDINGS.

By W. R. G. ATKINS, ScD., F.R.S.,
AND
H. H. POOLE, Sc.D.

[Read January 22. Published separately March 12, 1929.]

Introduction.

In recent years much attention has been devoted to a study of the illumination in buildings, mainly because the human factor in industrial output had to be considered seriously in view of the great strain imposed by the war upon munition workers. It was found that adequate illumination increased output through lessening eye-strain, and reduced the number of accidents.

Moreover, in 1890 Dr. T. A. Palm showed, by a geographical study of the incidence of rickets, that this disease is occasioned by inadequate light, especially sunlight. The idea was so novel that, like Mendel's famous discoveries concerning the laws of inheritance, it was ignored, and lost sight of. Later, other workers, from Buchholz in 1904 onwards, re-discovered the causal connection by quite different methods of attack. Since 1903 Rollier, in Leysin, has used light to combat tuberculosis. The most important radiation is, however, the ultra-violet, around 3,000 Å.U. This holds especially for rickets. Hill (1927) has shown, using an aqueous acetone solution of methylene blue exposed in a narrow quartz tube—placed vertically—as a roughly quantitative indication of the amount of ultra-violet radiation, that more of this may be received from the sky as a whole—especially from blue sky—than from the direct rays of the sun. This information was naturally cited by the firms selling glass transparent to the ultra-violet radiation of sun and skylight as a reason for installing such glass in positions inaccessible to direct sunlight. It is probable that this has been done in many instances, with the result that people in such rooms enjoy the comforting thought that they are receiving ultra-violet radiation. It will be seen in the sequel, however, that the fraction of the total diffuse skylight which reaches any point in a room [i.e., the "daylight factor" at the point] is usually very small, and the same will be true of the ultra-violet radiation, even if the window glass is almost perfectly transparent to the latter.

How small the daylight factor usually is will be evident from the tables which follow, but it may be said that this paper is being written at 3 p.m. on

December 13th, at a spot on a table where the daylight factor is 0·37 per cent.; the light is perfectly good for ordinary print, and permits one to read even the smallest print of an old prayer-book, published in 1801. Yet this position is only eight feet from the centre of a large north window, four feet in breadth and 7 feet 6 inches in height, reaching to the ground. In the window the daylight factor is only 7 per cent.; and on a path outside, midway to a high hedge, the daylight factor is 26·8 per cent. Across the road is a row of tall trees, but these are bare. In a similar large ground-floor east window the daylight factor is 7·2 per cent., or 14·6 when the photometer is sloped so as to give approximately a maximum value, denoted in the tables by M_s, the subscript denoting shade, viz., that the site is not exposed to the whole sky. When so exposed, $V = M$, obviously, for diffuse light. This window has a good east outlook, and fourteen feet from it the daylight factor on the grass was 64·9 per cent. There is, however, some shading from a Camellia bush against the wall to south of this east window. The photometer was on the floor, touching the window.

It may be seen, therefore, that with a daylight factor one per cent., which denotes quite a well-lighted position, one can receive but little ultra-violet radiation; thus, six minutes in the open is equivalent to 600 min., or ten hours indoors. Even in a greenhouse on a front bench the daylight factor for vertical illumination may not exceed about 25 per cent., while an apparently well-lighted position on the back wall may receive no more than 30 per cent., even with the photometer sloped to the maximum position.

It is obvious, therefore, that, unless a building is specially constructed for the purpose so as to be very well lighted, it is uneconomical to fit special glass, transparent to ultra-violet radiation, in positions other than those that receive direct sunlight. Such illumination would be totally inadequate in anti-rachitic action, nor could the influence upon general health exceed that due to a few minutes daily in the open air. In fact the presence of the ultra-violet-transmitting glass may give rise to a harmful delusion that the irradiation is adequate.

Methods of Measuring Indoor Daylight Illumination.

Walsh (1923) has summarised our knowledge of daylight and its variations, as determined from the illumination of test cards exposed horizontally in an open field at the National Physical Laboratory, direct sunlight being shielded from the cards. The mid-day vertical illuminations were found to vary from 58,430 metre candles in May to 1,400 in November, the mean monthly values being 44,130 for June, and 7,750 for December.

Paterson and Walsh (1915) showed that, on a dull day with a grey sky, the illumination at a point inside a building bears a very nearly constant ratio to the illumination at a point outside. This ratio, expressed as a percentage, has been termed the daylight factor at the point, and is taken as giving some indication of the illumination when the outside illumination is known.

The method used by Paterson and Walsh in this work, and used at the National Physical Laboratory, involved visual comparisons of brightness. The latest apparatus based on this principle is the Thorner Daylight Meter (Taylor, 1926). In this an image of a small portion of the sky is reflected on to a comparison screen; the brightness of this image is then varied by an iris diaphragm until it appears as bright as a test surface, viewed through a hole in the screen. Neutral filters are interposed if necessary.

The Macbeth Illuminometer (see Leeds and Northrup, 1920) has been used considerably in the U.S.A. for both indoor and outdoor measurements. It depends upon the visual comparison of daylight, reflected from a matt white surface, with the brightness of a translucent screen, illuminated by a small electric lamp run under standard conditions. The apparatus appears to be portable and convenient, though rather costly. Spare lamps should be kept, and used only for re-standardising the working lamp. The method of using a portable standard lamp is by no means new. Considerable use was made of it by Zederbaur (1907), near Vienna, in measuring light intensity, also the spectral distribution of the light, in various forest sites by the aid of Wingen's apparatus with a lamp burning the lighter distillates of petroleum.

The use of the photo-electric cell as a photometer has greatly increased of late years, with the advance which has been made in the construction of these cells. We have used both vacuum and gas-filled cells for some years for measuring submarine illumination (Poole, 1925; Poole and Atkins, 1926 and 1928), the current passing through a cell mounted in a strong case, and lowered into the sea, being measured, and also that through a cell exposed on the deck of a steam trawler. In the course of this and subsequent work a large number of measurements of full daylight were accumulated. These we hope shortly to collect and publish. Use was also made of the apparatus (Atkins and Poole, 1926) to study the illumination in a wood. Using two potassium vacuum photo-electric cells, connected to the current-measuring apparatus by cables, it was possible to make a series of readings of the vertical illumination in the open, and at various distances inside the wood. The results were expressed as percentages $\frac{V_s}{V_0}$, where these denote the vertical illumination in the shade and in the open. These values we termed daylight factors, δ, when determined in the absence of sunlight. It was ascertained that the lighting in a wood depended mainly on the general diffuse skylight; so, when the sun was out, it became necessary to allow for the fact that the photometer in the open received—the site being so chosen—full skylight plus sunlight, while that in the wood received a proportion of the diffuse skylight only, the effect of the direct sunlight being generally small. This allowance was made by shielding the photometer from direct sunlight by interposing a small object, so that as little as possible of the skylight was cut off. The illumination so obtained was closely the same as that found when a small dark cloud cut off the direct light

of the sun; such an occurrence effects but little alteration in the illumination of a point inside a wood. The ratio of the freely exposed to the shaded illumination thus determined is denoted as β. For full mid-September sunlight $\beta = 3{\cdot}5$ approx.; for a grey sky, or for a blue sky after sunset, $\beta = 1{\cdot}0$, by definition.

The foregoing examples illustrate the convenience of the use of a photo-electric cell for measuring daylight. What is actually measured is the photo-electric current. This, in the apparatus for use at sea, we measure by noting the fall in potential across a known high resistance, using a telephone with interrupter, condenser, and amplifier as a null point indicator with the potentiometer. There is, therefore, no personal factor such as is involved in the matching of luminosities. The bulk and weight of the apparatus constitute its only serious drawbacks.

The arrangement used at sea permitted the current to be measured down to 5×10^{-10} ampere, this being 0·5 of the potentiometer scale division. With a photometer (H) at 60 volts anode potential, 1 scale division, viz., 10^{-9} amp., corresponded to an illumination of 40 metre candles. Since even on a dull December day one may find the illumination to be at least 10,000 m.c., it is seen that one scale division corresponds to 0·4 per cent. of full daylight using this small vacuum cell. This would suffice for most ordinary ecological work, carried out in shady sites out-of-doors, but at sea more sensitive gas-filled cells were used for deep water. On the score of portability, however, another outfit had to be sought. The solution lay in the obtaining of a vacuum photo-electric cell sufficiently sensitive to be used with a portable galvanometer in shaded sites, or a micro-ammeter in the open.

Photo-electric Cells.

Photometer H contains a potassium vacuum cell, with a maximum colour sensitivity near or slightly below 4,000 Å.U., as shown in fig. 2 of our 1928 paper. It is mounted on the under side of the ebonite lid of a light-tight box, the pupil of the cell occupying a hole in the lid 1·4 cm. in diameter. The outer edge of this hole is steeply chamfered off, to admit low-angle light. The aperture is covered by a diffusing glass window, cemented to the outside of the lid.

The glass is opal-flashed on each surface, and is quite the best diffusing substance we have found as yet. It reduces the diffuse light, reaching the cell only by about one-half. Its effect on the colour-sensitivity curve is small. The cell was at first mounted with a guard wire, but this we found unnecessary for our work. Standardization was carried out against an open carbon arc lamp, as previously described by us (1928), for the standardization of photometer G, a similar, though less sensitive, potassium cell. The carbon arc was chosen as a standard since, of all those artificial sources which are readily

reproducible at any time, it most nearly resembles daylight in its spectrum energy distribution. As, however, the maximum sensitivity of the eye is in the yellow-green, whereas that of the cell is in the violet, daylight, which is considerably bluer than arc light, is appreciably brighter on the photo-electric scale than it is by visual comparison. This, however, is one of the fundamental difficulties inherent in the photometry of different light sources. It, of course, does not affect the values of the daylight factor, which are purely relative, provided that the colour of the light at the shaded site is unaltered. As mentioned previously, photometer H gave 10^{-9} amp. per 40 m.c. at 60 v. anode potential. For small changes in voltage a correction is applied by deducting 0·1 m.c. for every volt above 60, or by adding 0·1 m.c. for every volt below 60. This holds fairly well for voltages from 50–85, but it is preferable to keep between 60 and 70. In practice it has been kept between 57 and 63 volts.

The correction for the variation of reflection loss with obliquity was found to be very close to the theoretical value shown on p. 280 of our 1926 paper. For altitudes of incident "pure" sunlight from 90–50° the factor lies between 1·00 and 1·01. At 40° it is 1·02, at 30° 1·06, and at 20° 1·16. The value for diffuse light is 1·06, the same as for pure sunlight at 30°.

This cell, and that of photometer G, were obtained from the General Electric Company. Tests were carried out on G, also on L, a similar cell, mounted in a submarine photometer, and no change in sensitivity could be detected over a period of eight months, using a small test lamp, run at constant current, as described by us previously (1928). The lamp was reserved for the purpose.

Photometer H was only used in this work to calibrate two other photometers, B 188 and B 223, which were selected for use in the open and in the shaded situations, respectively.

The B photometers contain sodium vacuum cells, obtained from Dr. R. C. Burt, of Pasadena. They resemble electric lamp bulbs, and are mounted on standard radio valve sockets, with bayonet joints. The sodium has been deposited by electrolysis of the glass. Their large size and large aperture, and the perfection of the sodium film thus obtained, render them very sensitive, so that one can obtain the sensitivity usually sought by using a gas-filled cell, which, as is well known, is inconstant, and requires very frequent calibrations. The colour-sensitivity of the sodium cell is shown by Burt as having a maximum at about 3,600 Å.U. The two B photometers were constructed with opalised glass tops, 26·5 cm. × 21·5 cm., so as to take full advantage of the wide-angle illumination of the cell. No guard wire was used.

The B photometers were standardised against H, the currents being measured by a portable galvanometer and shunt (see fig. 1). The photometers were placed side by side in the open, commencing at 11.15 G.M.T. on September 27th, with a grey sky and east wind, the sun being scarcely visible through cloud. The lighting conditions were thus tolerably stable, but to get more correct values readings were made of H, B 223, and B 188 in quick succession. In all, five

readings were made with H and four with each of the others. From the averages of these, it appeared that B 188 was 19·4 times, and B 223 50·3 times as sensitive as H, so that 10^{-9} amp. corresponds to 2·06 m.c. with B 188, and only 0·795 m.c. with B 223. These figures are for an anode potential of 60 volts.

Galvanometers.

A portable galvanometer (Tinsley) with combined lamp and scale enclosed in a box, 21 × 14 × 14 cm., was used, in conjunction with a reversing switch and a 100,000 ohm Ayrton-Mather universal shunt (Gambrell), with B 223 to

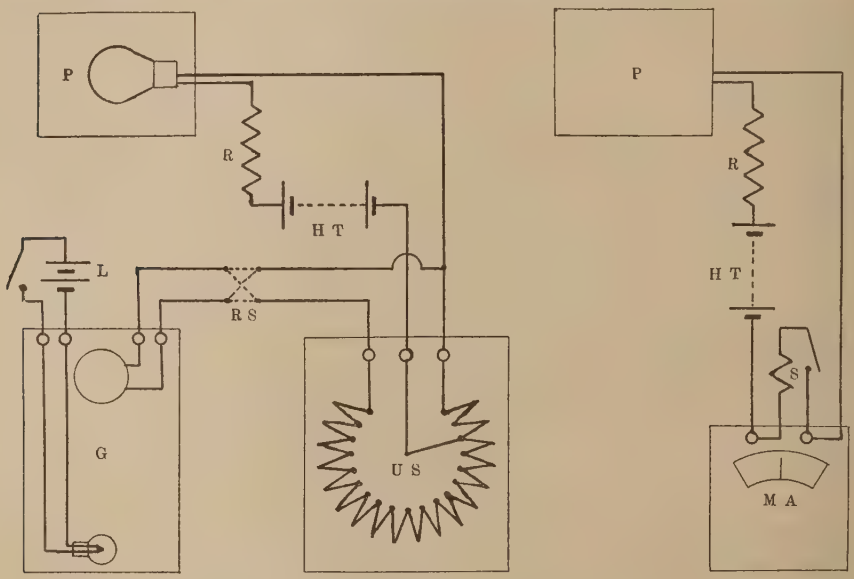

Fig. 1.

Arrangement of photometers and galvanometers at shaded base, left, and open base, right. L, galvanometer lamp battery. G, portable mirror galvanometer. RS, reversing switch. US, universal shunt. HT, high tension batteries, 60 volts. R, safety resistances, 10,000 ohms. P, photometers, the photo-electric cell is indicated in that on the left. MA, Onwood micro-ammeter. S, shunt, to one-fifth. For standardization of G, the P circuit was removed, and MA, with dry cell, connected to US instead. For comparison of the three photometers they were connected, in quick succession, to US, but only one is shown in figure.

measure the illumination in shaded sites. The connections are shown on the left in fig. 1, which shows also the two dry cells supplying the current for the galvanometer lamp, and a 10,000 ohm resistance, included in the photometer circuit as a precaution against accidental short circuits. The sensitivity of the galvanometer was found to be 12·5 scale divisions per micro-ampere, i.e., 25 scale divisions per μa on reversal. Readings could be estimated to 0·1 scale

division, which represents with B 223 an illumination of about 3·5 metre candles. The sensitivity was barely sufficient for some of the sites in the church. As the resistance of this galvanometer is 337 ohms, the use of the 100,000 ohm shunt in the 1/1 position only reduces the sensitivity to the extent of 0·3 per cent., while, by setting the shunt to 1/5, 1/50, or any desired ratio, any illumination can be measured readily. The variation in the resistance of the shunted galvanometer with the setting of the shunt is of no importance, as the reduction in the anode potential of the photometer caused by the potential difference across the shunt is too small to appreciably reduce the sensitivity. The same is true of the 10,000 ohm safety resistance.

For use in the open, even with the less sensitive photometer B 188, an Onwood type micro-ammeter (Gambrell) was sufficiently sensitive. This is divided to 0·5 μa, and can easily be read to 0·1 μa, corresponding to 206 m.c. For use in bright sunlight its sensitivity may be reduced to 1/5 by means of a suitable shunt, as shown on the right in fig. 1. The deflections can, if necessary, be doubled by the use of a reversing switch.

Method of Observation.

Instead of using two separate galvanometers the two photometers may be connected successively to the sensitive galvanometer and universal shunt, and alternate readings taken. This method enables the readings to be made by a single observer, but at least one pair of long well-insulated cables is required. For this purpose rubber-insulated high-tension ignition cable 8 mm. over-all diameter is used, any necessary joints being made by means of binding screws mounted on paraffin wax blocks.

As, however, in the present instance a pair of cables at least 100 metres long would have been needed, which would have been very inconvenient to handle, the photometers were connected to separate galvanometers, as already described, and read simultaneously by two observers. The illumination at the open site was read by one observer at minute or half-minute intervals, the exact times being noted, by means of photometer B 188 and the micro-ammeter. Meanwhile a second observer, with the more sensitive outfit, explored the illumination in the various shaded sites, noting also the exact times of the readings.

The open site is on the top of a garden wall about 3 metres high, in a commanding position on the top of a hill, at about the same level as the top of the tower of Antony Church, the illumination in which is shown in Table I, and well above the roof of the Old Vicarage, illuminations in which are shown in Tables II and III. The only obstructions to light are two rows of trees, one, at some distance, to the south-west, and the other, rather nearer but end-on, to the east. Both these rows cut off a little low-angle light.

The measurements were carried out with the anode potentials of both photometers as near 60 volts as was feasible, corrections being made for the small

alterations in sensitivity due to small differences in voltage. These were obtained from data supplied by Dr. Burt. For B 223 the correction is 0·5 per cent., and for B 188 it is 0·2 per cent. per volt. The corrections are to be deducted from the value for metre-candle sensitivity at 60 volts, if the actual voltage exceeds that amount.

The Effect of Sunlight in Shaded Sites.

As the daylight factor of a shaded sight has been defined with reference to diffuse light only, the effect of direct sunlight must be considered. The photometer in the open receives both diffuse and direct light, if the sun be shining. The shaded site is, on the other hand, often but little affected by direct sunlight. This is true for any part of a room through the windows of which no sunlight passes, and is found to be also true for most sites in woods, provided that no beams of direct sunlight occur in the immediate vicinity. If, however, sunlight enters the room, or the part of the wood near the site, the illumination will be increased by reflected sunlight.

All the indoor sites described in the sequel were, at least approximately, unaffected by direct sunlight at the time of measurement, so, in finding the daylight factor, allowance had, sometimes, to be made, as described below, for the effect of direct sunlight on the photometer in the open.

The Illumination in Buildings.

A careful comparison of the illumination obtaining in buildings of various architectural styles might in itself prove instructive. As a beginning, the vertical and (approximately) maximum illuminations were determined at twenty-eight sites in Antony Church (see plan, fig. 2). The order of the positions was arranged with the object of avoiding the pillars, five on each side, so that the photometer could conveniently be moved from one site to another without disconnecting the cables from the measuring apparatus, which was set up on a board resting on two pew-tops near the middle of the church.

The church contains a fine bronze, dated 1420, in the chancel, so it must be older than that. It is said that the north aisle is of later date than the rest of the building, of which the tower at least dates from about 1280. Between the side aisles and the nave there are six arches, of which the two at the north-east are unsymmetrical with respect to the south-east pair. There are seventeen windows, all of stained glass, save the west window, under the tower, and the south-west window. These, especially the latter, are the chief sources of light in the building. All windows, save two very small ones on each side of the chancel, have stone-work septa, dividing the glass into three main portions, with smaller areas above in most of them. There are four windows on the south side and five on the north. The latter are about 5 feet above floor level, the former about 6 feet. The ground slopes down towards the church on the south

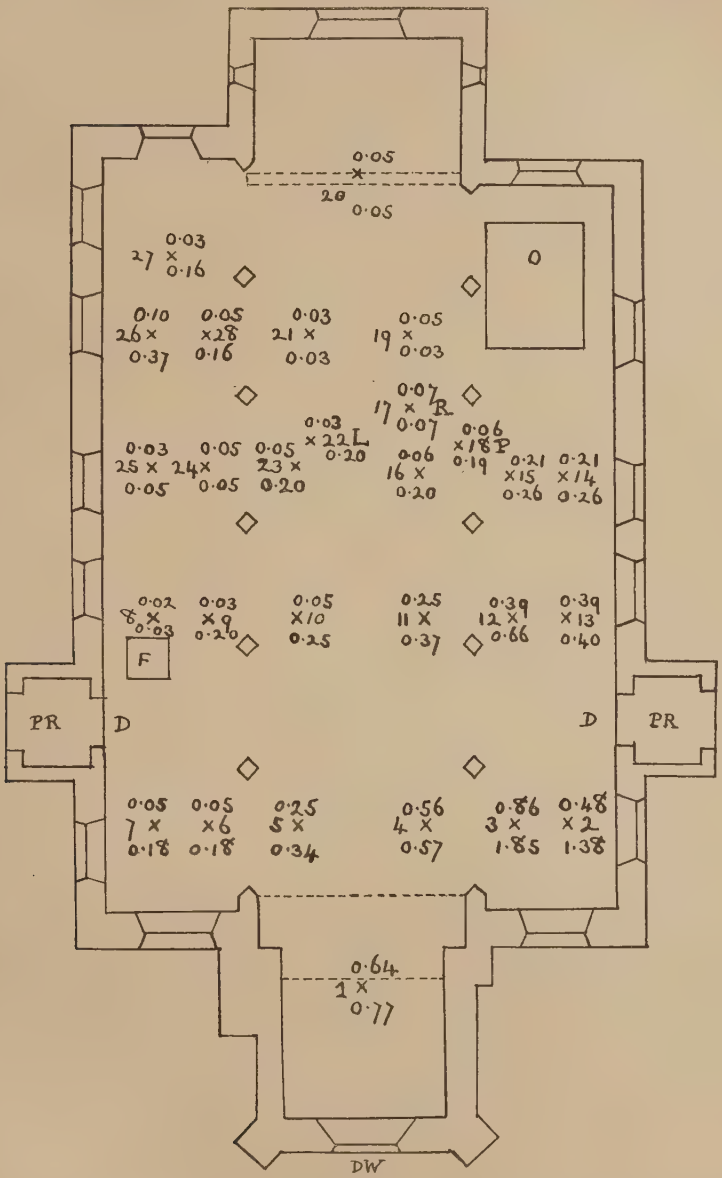

FIG. 2.

Plan of interior of Antony Church. Positions of numbered sites marked X; the figures above X are the values of the daylight factor, δ; the figures below X are the values for δ_M, photometer being sloped approximately to position of maximum illumination. F, font. O, organ in S.E. corner. L, lectern. R, reading desk. P, pulpit. D, door. DW, west door, under west window, beneath tower. PR, porch. Measurements made with doors shut.

side, but the north has a wide outlook—with few trees—also the east. In the west the ground rises somewhat, and to N.W. there are trees quite close, also more distant trees to S., S.W., and W. The west window is about 11 feet above the floor of the tower (vestry), which is five steps, about 3 feet 6 inches above the main floor. The dotted lines in the plan indicate the limits of the steps. The window is about 5 feet wide, and appears to be about 10 feet high. All windows have bevelled edges in the thick masonry. The other important window, in the S.W., is about 9 feet up, 5 feet wide, and about 10 feet high. The window heights were not measured.

Table I shows the illuminations found. The columns show respectively:—The site number; the condition of the sky; the ratio of sun plus sky to sunlight, viz., β; the illumination in the open, V_0; the vertical illumination V_s, and the maximum M_s, at the shaded site. The next two columns record percentage values of $\frac{V_s}{V_0}$ and $\frac{M_s}{V_0}$. In the absence of direct sunlight these are the vertical and maximum daylight factors, respectively. As, however, the sun was shining part of the time two other columns are given, $\frac{V_s\beta}{V_0} = \delta$, the true daylight factor and $\frac{M_s\beta}{V_0} = \delta_M$, the daylight factor derived from comparing the maximum reading at the shaded site with V_0.

Values of β could not be determined separately for each reading, since this necessitates two workers at the open base. It was not, however, necessary for the conditions under which we worked. From the values of β found, the intermediate values were interpolated—these being shown in square brackets; the interpolation was effected with due regard to the variations in the general lighting conditions and their daily trend.

It remains to consider the reflection-loss factor "f" used in these measurements. The vertical light in the church—and in the house—was taken as uniformly diffused, at any rate it was mostly at a low angle; accordingly the appropriate factor, 1·06, was used to multiply the sensitivity factor of the photometer. For values of M_s however the light was considered to be vertical, or between the vertical and 50°, accordingly the factor 1·00 used.

In the open, with sun obscured, the factor is obviously 1·06 also. At noon on November 9th the altitude of the sun is approximately 24°; for pure sunlight, therefore, the factor should be 1·10. The pure sunlight was, however, only 0·8 of the diffuse light, accordingly the factor should be:—

$$\frac{1{\cdot}06 \times 1 + 1{\cdot}10 \times 0{\cdot}8}{1{\cdot}8} = 1{\cdot}08,$$

almost; with $\beta = 1{\cdot}6$ the weighted factor is 1·07. There was, however, a considerable amount of high-angle light from clouds, so for simplicity the diffuse light factor, 1·06, was used in all the calculations of illumination at the open

base—on the wall—on November 9th. In the afternoon the values of β were so low that it seemed simpler to neglect the effect of the sunlight upon the angular distribution of the light. It is obvious that this correction is always an uncertain one, though fortunately it is comparatively small—very small indeed compared to the rapid fluctuations in daylight. It will be noticed in Table I that all the measurements of illumination in the church were made in less than an hour. The plan shows the distribution of light, vertical and maximum values of the daylight factor being marked. The measurements were made with the photometer at the level of the tops of the pews, or at book level for pulpit, lectern, and reading desk.

The values found are throughout very low. On the visual scale, they are perhaps rather too low, because it is possible that the stained glass may have altered the spectral distribution of the light, so that the blue, to which the cell used is most sensitive, may have been reduced proportionally more than the red end of the spectrum. There is some blue glass in the windows, but it is a dark blue, that stops a high percentage of the light.

The smallness of the daylight factor in the church, and in buildings in general, may occasion surprise. The church examined is undoubtedly rather a dark one, but the illuminations at the positions—near large windows—in the house are by no means abnormal; these are shown in Tables II and III. It must, however, be remembered that, normally, the eye is set vertically; it does not receive the full light of the sky. How great this is can be judged from the brightness of those street signs which have become so common within the last few years; in these, skylight is reflected through coloured lettering. Again, very few ordinary positions in towns, and near dwellings, receive the whole skylight. The eye, moreover, adapts itself very quickly to variations in illumination. For example, on entering a wood of deciduous trees on an autumn day, with bright sunlight, one is only aware of a restful feeling; no very great diminution in light is noted. Further in, the grass has disappeared, and trailing ivy may have become a conspicuous feature on the ground. In such a site we have found (1926) a daylight factor of one to two per cent., which means less than one per cent. of the illumination in full sunlight. Again, however, it must be mentioned that the spectral character of the light may have—has certainly in fact—changed somewhat, so that the visual brightness is rather greater than that indicated by the blue-sensitive cell. It is, indeed, the same sort of difference in the character of the light that occasions difficulty in judging correct photographic exposures under certain conditions. The photo-electric cell is a far better judge of the light intensity, as it relates to a photographic plate, than is the eye.

The results of Table I are best studied with the aid of the plan (fig. 2), which shows the values of δ above and δ_M below the numbers denoting the different sites. These records show, respectively, maxima of 0·86 and 1·85, and minima of less than 0·02 and 0·03.

TABLE I.

Antony Church, 11.40 a.m.–12.35 p.m., November 9, 1928.—Clear sun, blue sky, a few clouds, wind N.E., light. Frost on grass in shade till 10.30 a.m.

Site.	Condition of sky.	β	Illumination in metre candles. In open. V_0	In shade. V_s	In shade. M_s	Percentage. $\frac{V_s}{V_0}$	$\frac{M_s}{V_0}$	Daylight factor = δ. $\frac{V_s\beta}{V_0} = \delta$	$\frac{M_s\beta}{V_0} = \delta_M$
1	A few clouds around sun ...	1·8	30,000	109	—	0·36	—	0·64	—
1	" " " " ...	"	30,100	—	131	—	0·43	—	0·77
2	" " " " ...	"	30,100	82	—	0·27	—	0·48	—
2	" " " " ...	"	30,300	—	233	—	0·77	—	1·38
3	" " " " ...	"	30,600	146	—	0·48	—	0·86	—
3	" " " " ...	"	32,000	—	330	—	1·03	—	1·85
4	" " " " ...	"	33,100	102	—	0·31	—	0·56	—
4	" " " " ...	"	32,800	—	106	—	0·32	—	0·57
5	" " " " ...	"	32,300	45	—	0·14	—	0·25	—
5	" " " " ...	"	32,900	—	64	—	0·19	—	0·34
6	" " " " ...	"	33,400	11	—	0·03	—	0·05	—
6	" " " " ...	"	33,100	—	32	—	0·10	—	0·18
7	Cloud reflecting near sun ...	"	34,200	11	—	0·03	—	0·05	—
7	" " " " ...	"	34,400	—	32	—	0·10	—	0·18
8	" " " " ...	"	32,700	< 7	—	< 0·02	—	< 0·03	—
8	Cloud reducing light ...	"	31,600	—	11	—	0·03	—	0·05
9	" " " ...	"	31,800	7	—	0·02	—	0·03	—
9	" " " ...	"	32,300	—	35	—	0·11	—	0·20
10	" " " ...	"	31,800	11	—	0·03	—	0·05	—
10	" " " ...	"	30,500	—	42	—	0·14	—	0·25
11	Cloud over sun	1·0	17,800	45	—	0·25	—	0·25	—
11	" " "	[1·1]	20,500	—	70	—	0·34	—	0·37
12	Sun clear	[1·7]	29,600	68	—	0·23	—	0·39	—
12	" "	"	30,700	—	128	—	0·42	—	0·66
13	" "	"	29,600	68	—	0·23	—	0·39	—
13	Cloud over sun	[1·1]	19,200	—	70	—	0·36	—	0·40
14	" " "	1·0	17,200	37	—	0·21	—	0·21	—
14	" " "	"	17,200	—	45	—	0·26	—	0·26
15	Sun's disc just visible ...	"	17,400	37	—	0·21	—	0·21	—
15	" " " " ...	"	17,600	—	38	—	0·22	—	0·26
16	" " " " ...	"	17,400	11	—	0·06	—	0·06	—
16	Sun emerging	[1·5]	27,500	—	35	—	0·13	—	0·20
17	Sun through light cloud ...	[1·7]	28,800	11	—	0·04	—	0·07	—
17	Sun clear	"	31,100	—	11	—	0·04	—	0·07
18	Sun through cloud	[1·2]	20,300	11	—	0·05	—	0·06	—
18	Sun almost clear	[1·6]	28,300	—	35	—	0·12	—	0·19
19	Bright clouds, clear sun ...	[1·7]	32,700	11	—	0·03	—	0·05	—
19	" " " " ...	"	32,900	—	7	—	0·02	—	0·03
20	" " " " ...	"	34,900	11	—	0·03	—	0·05	—
20	" " " " ...	"	35,900	—	11	—	0·03	—	0·05
21	Clear sun	"	35,900	7	—	0·02	—	0·03	—
21	" "	"	35,900	—	7	—	0·02	—	0·03
22	" "	"	33,800	7	—	0·02	—	0·03	—
22	" "	"	32,100	—	38	—	0·12	—	0·20
23	" "	[1·6]	32,100	11	—	0·03	—	0·05	—
23	" "	"	31,600	—	38	—	0·12	—	0·20
24	" "	"	31,100	11	—	0·03	—	0·05	—
24	" "	"	31,600	—	11	—	0·03	—	0·05
25	" "	"	32,700	7	—	0·02	—	0·03	—
25	" "	"	31,000	—	11	—	0·03	—	0·05
26	Sun's disc visible	[1·1]	19,600	11	—	0·06	—	0·06	—
26	" " "	[1·2]	20,700	—	64	—	0·31	—	0·37
27	Sun almost clear	1·6	29,000	7	—	0·02	—	0·03	—
27	Sun clear	"	35,900	—	35	—	0·10	—	0·16
28	" "	"	34,300	11	—	0·03	—	0·05	—
28	" "	"	33,800	—	35	—	0·10	—	0·16

Table II shows the illuminations in a room well provided with windows. This was the room mentioned near the beginning of this paper, in which the large north window faced a row of bushes, with nearly bare trees across a road, the daylight factor on a path opposite it being 26·8 per cent. Another window in the south-east corner of the room was situated in a built-out recess, which had small side windows also. In the open, about five yards away, the daylight factor was 47·6 per cent., since to the west the house shaded it, and to the north evergreen trees and bushes. The walls of the room were light blue distemper, with white woodwork, but dark furniture. The values of δ were from 1·1–0·27 per cent. on a large central table, δ_M being 1·3–0·53 per cent., neglecting one erroneously low value.

TABLE II.

Old Vicarage, Antony, 2.35–3 p.m., November 9, 1928.—Sky clear to N.; sun behind cloud in S.W., then through white clouds. $\beta = 1{\cdot}16$ at 3.7 p.m. and $\beta = 1{\cdot}09$ at 3.38. Dining-room, woodwork white, dark furniture, walls light blue distemper. North window 4 ft. by 7 ft. 6 in., reaching to ground; east window in 4 ft. recess, 3 ft. 8 in. × 6 ft., at 2 ft. 10 in. above floor level; also side panel windows in recess, 10 in. × 6 ft.

		Illumination in metre candles.			Percentages.			
							Daylight factor = δ.	
	β	V_0	V_s	M_s	$\frac{V_s}{V_0}$	$\frac{M_s}{V_0}$	$\frac{V_s\beta}{V_0} = \delta$	$\frac{M_s\beta}{V_0} = \delta_M$
North window, photometer on floor ...	1·0	12,200	850	—	7·0	—	7·0	—
" " " " " ...	"	12,200	—	1060	—	8·7	—	8·7
On 2 ft. 4 in. table, N. side, 6 ft. from N. window	"	12,300	136	—	1·1	—	1·1	—
" " " " " "	"	12,300	—	160	—	1·3	—	1·3
On table, S. side, 8 ft. from N. window and 14½ ft. from E. recess window	"	12,500	34	—	0·27	—	0·27	—
" " " " " "	"	12,600	—	67	—	0·53	—	0·53
On table, E. end, 7 ft. from N. window and 13 ft. from E. window	[1·1]	13,200	48	—	0·36	—	0·40	—
" " " " " "	[1·2]	14,200	—	96	—	0·68	—	0·79
On table, W. end, 8 ft. from N. window and 17½ ft. from E. window	"	13,600	44	—	0·32	—	0·37	—
" " " " " "	"	14,200	—	43	—	0·30	—	0·35*
East window, on floor	"	13,700	388	—	2·8	—	3·2	—
" " " "	"	13,800	—	432	—	3·1	—	3·6

* Sloped photometer was evidently not pointed in most advantageous direction in this case.

As compared with the north room of Table I, the east room of Table II has relatively better lighting. This is, apparently, because of its more open aspect,

so that while δ is almost the same in each of the floor-level windows, yet that facing east shows δ_M 14·6 as against 8·7 per cent.

The south room faces rising ground, with trees, and the window, reaching to floor-level, is somewhat shaded by bushes and climbers. Though the value of δ is 59 per cent. in the open, five yards away, the aspect is not good. The interior values of δ are very low. The kitchen, on the other hand, with a north window is better illuminated than one would expect, partly due to whitewashed walls outside the window.

TABLE III.

Old Vicarage, Antony, 3.9–3.30 p.m., November 9.—Sky as in Table II. Drawing-room, woodwork white, dark furniture, walls light blue distemper. East window, floor level.

Also hall, on table under small west window; white woodwork, light blue distemper, 3.21. Study, white woodwork, dark furniture, walls light blue distemper, 3.25–3.28. South window, floor level. Kitchen, white woodwork, cream-coloured distemper, 3.30 p.m. North window, at level of table.

		Illumination in metre candles.			Percentages.			
	β	V_0	V_s	M_s	$\frac{V_s}{V_0}$	$\frac{M_s}{V_0}$	$\frac{V_s\beta}{V_0} = \delta$	$\frac{M_s\beta}{V_0} = \delta_M$
In open at 3.7 p.m.	1·2	12,600	—	—	—	—	—	—
East window, photometer on floor of drawing-room	[1·2]	12,000	748	—	6·25	—	7·2	—
„ „ „ „ „	„	11,300	—	1,440	—	12·70	—	14·6
On 2 ft. table, 10 ft. from window ...	[1·1]	10,800	102	—	0·94	—	1·1	—
„ „ „ „ ...	„	10,700	—	173	—	1·62	—	1·8
On stool, 21 ft. from window ...	„	10,300	34	—	0·33	—	0·37	—
„ „ „ „ ...	„	10,100	—	48	—	0·47	—	0·53
Hall, west window, yellow and frosted glass	„	9,900	34	—	0·34	—	0·38	—
„ „ „ „ „	„	9,600	—	38	—	0·40	—	0·45
Study, 3 ft. from window (south), on table	„	9,500	146	—	1·54	—	1·71	—
„ „ „ „ „	„	9,400	—	237	—	2·53	—	2·81
Study, on writing-desk, 8 ft. 6 in. diagonally from window	„	9,300	7	—	0·08	—	0·09	—
„ „ „ „ „	„	9,200	—	11	—	0·12	—	0·13
Kitchen, on chair, by range, 12 ft. from window	„	8,900	34	—	0·38	—	0·42	—
„ „ „ „ „	„	8,700	—	43	—	0·49	—	0·54
Kitchen, on table, 3 ft. 6 in. from window (north)	„	8,500	204	—	2·40	—	2·64	—
„ „ „ „ „	„	8,300	—	266	—	3·22	—	3·5
In open at 3.38 p.m.	1·1	7,600	—	—	—	—	—	—

It may be added that we made measurements to test the constancy of δ for a shaded situation out of doors. These will be shown in a forthcoming ecological paper. As might be expected, the value varies somewhat, but not enough to impair its utility for purposes of comparison.

In conclusion, we desire to acknowledge our indebtedness and to express our thanks as follows:—To Ingaborg Atkins, for much help in reading the galvanometers; to the Rev. G. H. Miller, M.A., Vicar of Antony, for permission to make measurements in the church; to the Government Grant Committee of the Royal Society, for enabling us to purchase the photo-electric cells and other apparatus; to the Royal Dublin Society, for laboratory facilities, and apparatus used in standardizing: to the Marine Biological Association of the United Kingdom, for the use of apparatus, and for facilities at the Plymouth Laboratory.

Summary.

1. By the use of vacuum sodium photo-electric cells of the Burt type, together with suitable portable galvanometers, simultaneous measurements were made of the illumination in the open and in a building; the ratio expressed as a percentage, the daylight factor, is a useful index of the illumination inside buildings.

2. In Antony Church the values of the daylight factor varied from under 0·02 to 0·86 per cent. for vertical illumination; or, with photometer sloped to receive maximum illumination, from under 0·03 to 1·85. The church dates from before 1420 A.D.

3. In the dwelling-house examined, the daylight factor immediately inside large windows is close to 7·2 for vertical light, rising to 14·6 for sloped position. The value in a well-lighted room is under one per cent. From this it follows that it is uneconomical to fit glass transparent to ultra-violet light in windows other than those that receive direct sunlight, save in buildings specially constructed to admit a far larger proportion of skylight than is customarily the case.

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No. 19.

CONIFERAE: KEYS TO THE GENERA AND SPECIES, WITH ECONOMIC NOTES.

By H. M. FITZPATRICK, B.Agr.Sc.

(Plates 9–15.)

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INTRODUCTION.

The family Coniferae is an extensive one, comprising forty-seven genera and four hundred and ninety living species. It is widely distributed throughout the northern and southern hemispheres at the present day, and occurs plentifully in the fossil state. The Conifers are woody plants, usually large trees growing in forests, and many of them are economically important for timber, and as sources of resins, turpentine, pitch, aromatic oils, wood-pulp and paper. Their wood is extensively employed in manufacture and construction, and, owing to this and the speedy rate at which they grow, certain species of Conifers are cultivated on a large scale commercially.

Botanically, the Conifers belong, with the Cycads and Ginkgo, to the Gymnosperms. They are monoecious or dioecious, with unisexual flowers, the male ones consisting of antheriferous scales collected in early deciduous cones, and the female either of imbricated carpels arising from the axil of a bract, and bearing one or more naked ovules on the upper face, or of a solitary naked ovule, terminal or in the axil of a bract. The fruit is either many-seeded, with the seeds borne on woody or fleshy scales, or one-seeded, the seed being enclosed in a succulent or fleshy envelope. The wood of the stem consists entirely of tracheids and xylem-parenchyma. The leaves are very variable in size and structure, ranging from large, ovate or lanceolate to minute and scale-like, in most cases having marked zerophytic characters.

The present work was undertaken with the object of compiling a comprehensive series of descriptions of the species of the Coniferae, based on the morphology of the foliage, arranged in the form of an artificial key. In the recognition of plants, in the living or in the fossil state, the characters of the flowers or fruit are often of no help, as these may not be available. Living trees must be identified by means of peculiarities of the foliage alone in youth, and later in life also if they are not bearing cones. Workers in palæobotany

recognise fossil remains of plants in many cases by the impressions of leaves and twigs, and for such work keys are essential. Obvious characters, which can be made out with the naked eye or by the use of a pocket lens, are as far as possible relied upon in the descriptions. The main divisions of the key rest upon the arrangement of the leaves of normal sterile branches, occurring in the lower part of the crown of adult trees, and on their shape and their mode of attachment to the twigs. In the Abietineae the twigs become woody in the second year of growth, and this distinguishes this important timber-producing tribe from all other Conifers except Taxodium.

Certain genera may be recognised at a glance by some prominent character. Pinus has long needle-like leaves in clusters of from two to five. Sciadopitys, with its long, grooved cladodes arranged in regular whorls, is unmistakable. Larix and Pseudolarix have light green leaves in clusters on spurs, and are, with Taxodium and Glyptostrobus, the only genera which are deciduous, the latter two being distinct by their annual branchlets falling with the leaves in autumn.

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CLASSIFICATION.

ABIETINEAE.

1. *Picea,* Dietrich. 38 species, North Temperate Zone.
2. *Tsuga,* Carrière. 9 species, Japan, Formosa, China, Himalaya, and North America.
3. *Pseudotsuga,* Carrière. 7 species, Western North America, Western China, Japan, and Formosa.
4. *Abies,* Linnaeus. 37 species, North Temperate Zone.
5. *Keteleeria,* Carrière. 3 species, China, Japan, and Formosa.
6. *Cedrus,* Lawson. 4 species, Atlas Mountains, Himalaya, Syrian Mountains, and Cyprus.
7. *Larix,* Adanson. 18 species, North Temperate Zone.
8. *Pseudolarix,* Gordon. 1 species, Eastern China.
9. *Pinus,* Linnaeus. 80 species, Temperate Northern Hemisphere, West Indies, Central America, and Philippines.

ARAUCARINEAE.

10. *Agathis,* Salisbury. 16 species, New Zealand, Australia, New Caledonia, Fiji, Philippines, Malaya.

11. *Araucaria,* Jussieu. 10 species, Australia, New Guinea, New Caledonia, New Hebrides, Norfolk Island, S. America.
12. *Cunninghamia,* R. Brown. 2 species, China, Formosa, and Japan.
13. *Taiwania,* Hayata. 1 species, Formosa and South-Western China.

TAXODINEAE.

14. *Athrotaxis,* D. Don. 3 species, Tasmania.
15. *Sequoia,* Endlicher. 1 species, California.
16. *Wellingtonia,* Lindley. 1 species, California.
17. *Cryptomeria,* D. Don. 1 species, China and Japan.
18. *Glyptostrobus,* Endlicher. 1 species, Southern China.
19. *Taxodium,* L. C. Richard. 3 species, South-Eastern United States, and Mexico.
20. *Sciadopitys,* Siebold and Zuccarini. 1 species, Japan.

CUPRESSINEAE.

21. *Cupressus,* Linnaeus. 17 species, North Temperate Zone.
22. *Thuya,* Linnaeus. 5 species, China, Japan, Korea, and North America.
23. *Biota,* Endlicher. 1 species, China.
24. *Microbiota,* Komarov. 1 species, Eastern Siberia.
25. *Libocedrus,* Endlicher. 6 species, South-Western China, Formosa, New Zealand, and South America.
26. *Fokienia,* Henry and Thomas. 1 species, China.
27. *Thujopsis,* Siebold and Zuccarini. 2 species, Japan.
28. *Juniperus,* Linnaeus. 35 species, Northern Hemisphere, East Africa.
29. *Fitzroya,* J. D. Hooker. 1 species, Tasmania.
30. *Diselma,* J. D. Hooker. 1 species, Tasmania.
31. *Callitris,* Ventenat. 18 species, Australia and Tasmania.
32. *Actinostrobus,* Miquel. 2 species, Western Australia.
33. *Widdringtonia,* Endlicher. 5 species, Africa.
34. *Tetraclinis,* Masters. 1 species, North Africa.
35. *Callitropsis,* Compton. 1 species, New Caledonia.

TAXACEAE.

36. *Taxus,* Linnaeus. 7 species, North Temperate Zone.
37. *Austrotaxus,* Compton. 1 species, New Caledonia.
38. *Amentotaxus,* Pilger. 1 species, China.
39. *Torreya,* Arnott. China, Japan, and Southern United States.
40. *Cephalotaxus,* Siebold and Zuccarini. 6 species, China, Japan, Khasia Mountains, and Assam.
41. *Pherosphaera,* Archer. 2 species, Tasmania and New South Wales.

42. *Dacrydium,* Solander. 18 species, Malaya, Philippines, New Guinea, New Caledonia, New Zealand, South America, and Tasmania.
43. *Acmopyle,* Pilger. 1 species, New Caledonia.
44. *Podocarpus,* L'Héritier. 70 species, Tropics and Sub-Tropics, mostly Southern Hemisphere.
45. *Saxegothaea,* Lindley. 1 species, Chile.
46. *Microcachrys,* J. D. Hooker. 1 species, Tasmania.
47. *Phyllocladus,* L. C. Richard. 6 species, Tasmania, New Zealand, Philippines, New Guinea, and Borneo.

KEY TO THE GENERA.

(The numbers refer to the Classification.)

I.—LEAVES SPIRALLY ARRANGED ON THE TWIGS.

A.—TWIGS WOODY IN THE SECOND YEAR: LEAVES LINEAR.

I.—LEAVES SOLITARY.

4. *Abies.*—Silver firs. Leaves keeled on the lower side only, leaving when they fall circular scars on the twigs. Plate 9, fig. 1.

5. *Keteleeria.*—Leaves keeled on both sides, leaving when they fall circular scars on the twigs. Plate 9, fig. 2.

3. *Pseudotsuga.*—Douglas firs. Leaves arising from coloured slightly prominent bases, and leaving when they fall oval scars on the twigs. Buds spindle-shaped, sharp-pointed, with shining brown scales. Plate 9, fig. 3.

1. *Picea.*—Spruces. Leaves arising from peg-like projections on the twigs. Plate 9, fig. 4.

2. *Tsuga.*—Hemlock firs. Leaves arising by a slender stalk which lies pressed against the twig. Plate 9, fig. 5.

Taxodium.—Branchlets deciduous. See No. 19.

II.—LEAVES IN CLUSTERS OF 2, 3, 4, or 5.

9. *Pinus.*—Pines. Leaves long and needle-like. Plate 9, fig. 6.

III.—LEAVES IN CLUSTERS OF 15–60 ON SHORT SPURS; SINGLE AND SCATTERED ON THE LONG SHOOTS WHICH CONTINUE GROWTH.

7. *Larix.*—Larches. Leaves soft, annual, deciduous in autumn. Spurs short without persistent scales. Buds with short appressed scales. Plate 9, fig. 7.

8. *Pseudolarix.*—Golden larch. Leaves soft, annual, deciduous in autumn. Spurs long with thread-like scales. Buds with long awl-like scales. Plate 9, fig. 8.

6. *Cedrus.*—Cedars. Leaves stiff, tetragonal, perennial. Plate 10, fig. 9.

B.—TWIGS REMAINING GREEN AND NON-WOODY IN THE SECOND YEAR.

I.—LEAVES SCALE-LIKE, COVERING ENTIRELY THE AXIS OF THE TWIG.

(I.)—Margin of the leaves opaque and entire.

42. *Dacrydium Franklini, D. Bidwillii* and *D. biforme.* — Leaves closely appressed, angular on the back with scattered stomatic lines; apex acute or obtuse. Plate 10, fig. 10.

44. *Podocarpus dacrydioides.*—Leaves slightly spreading, convex and keeled on the back, without visible stomatic lines; apex mucronate, incurved. Plate 10, fig. 11.

(II.)—Margins of the leaves translucent and finely serrate.

14. *Athrotaxis cupressoides.*—Leaves closely appressed, angular on the back with indistinct stomatic lines; apex acute. Plate 10, fig. 12.

41. *Pherosphaera Hookeriana.*—Leaves closely appressed, convex on the back without visible stomatic lines; apex rounded. Plate 10, fig. 13.

II.—LEAVES CURVED, DECURRENT AND BROAD AT THE BASE, GRADUALLY NARROWING TOWARDS THE APEX.

17. *Cryptomeria.*—Leaves tetragonal, with stomata on all four surfaces and a large central resin-canal; apex sharp-pointed. Plate 10, fig. 14.

13. *Taiwania.*—Leaves trigonous, with distinct stomatic bands on all three surfaces and a large central resin-canal; apex incurved, mucronate. Plate 10, figs. 15 and 16.

16. *Wellingtonia.*—Leaves trigonous, with indistinct stomatic lines on the back; ventral surface with a green midrib and two stomatic bands; central resin-canal; apex tapering to a sharp point. Plate 10, fig. 17.

11. *Araucaria*: Section *Eutassa.*—Leaves only slightly decurrent, oval or quadrangular in cross-section, with resin-canals scattered through the substance of the leaf; stomatic lines variable; apex acute. Plate 10, fig. 18.

14. *Athrotaxis selaginoides* and *A. laxifolia.*—Leaves only slightly decurrent, rigid, trigonous, with two lateral stomatic depressions on the dorsal surface near the base; central resin-canal; apex sharp-pointed. Plate 10, figs. 19 and 20.

41. *Pherosphaera Fitzgeraldii.*—Leaves trigonous, without stomatic lines on the back; ventral surface with a single stomatic band; apex mucronate. Plate 10, fig. 21.

43. *Acmopyle.*—Leaves flattened, oval in cross-section; apex blunt or sharp-pointed; upper surface with scattered indistinct stomatic lines; lower surface with two broad stomatic bands. Plate 10, fig. 22.

III.—LEAVES LINEAR, FLAT.

(I.)—BRANCHLETS AND LEAVES PERENNIAL, *i.e.*, PERSISTING MORE THAN ONE YEAR.

(a) **Leaves with two conspicuous stomatic bands on the lower surface; resin-canal central.**

(*a*) *Branchlets alternate.*

15. *Sequoia sempervirens.*—Bud scales persistent at the base of the annual branchlets. Leaves decurrent; upper surface convex, with a median groove; apex acuminate with a sharp cartilaginous point. Plate 10, fig. 23.

44. *Podocarpus andinus* (*Prumnopitys elegans*).—Bud scales all deciduous or a few persistent and inconspicuous. Leaves shortly stalked; upper surface convex with an inconspicuous midrib; apex acute with a short horny point. Plate 11, fig. 24.

(*b*) *Branchlets opposite, sub-opposite, or in whorls of three or four.*

45. *Saxegothaea.*—Leaves acute, mucronate; upper surface convex; midrib prominent on both surfaces. Plate 11, fig. 25.

44. *Podocarpus nubigenus.*—Leaves acuminate, with a sharp cartilaginous point; upper surface convex; midrib prominent on both surfaces. Plate 11, fig. 26.

39. *Torreya.*—Leaves acuminate, with a long bristle-like point; upper surface convex, with an indistinct midrib; lower surface with a prominent midrib and two longitudinal stomatic grooves. Plate 11, fig. 27.

40. *Cephalotaxus.*—Leaves acute, with a short spine-like point; upper surface with a prominent midrib sunk in a depression. Plate 11, fig. 28.

38. *Amentotaxus.*—Leaves acuminate, with a short point; upper surface convex, with a prominent midrib; lower suface with marginal green bands, equalling in breadth the glaucous stomatic bands. Plate 15, fig. 67

(b) **Leaves without conspicuous stomatic bands.**

(*a*) *Leaves with a prominent midrib on the upper surface.*

36. *Taxus.*—Yews. Leaves without a resin-canal, shortly stalked, convex above, and with indistinct stomatic lines beneath. Plate 11, fig. 29.

(*b*) *Leaves with a median groove on the upper surface.*

37. *Austrotaxus.*—Leaves up to 4 in. long, with recurved margins and a blunt point. Plate 15, fig. 58.

44. *Podocarpus Totara* and *P. Hallii.*—Leaves up to 1½ in. long, with flat margins and a sharp cartilaginous point. Plate 11, fig. 30.

(II.)—BRANCHLETS OF TWO KINDS, ANNUAL AND PERENNIAL, THE FORMER FALLING WITH THE LEAVES IN THE AUTUMN OF THE FIRST YEAR.

18. *Glyptostrobus.*—Chinese Swamp Cypress. Perennial branchlets remaining green for several years, and bearing white stomatic dots. Plate 11, fig. 31.

19. *Taxodium.*—American Swamp Cypress. Perennial branchlets becoming brown and corky in the second year, and without visible stomatic dots. Plate 11, fig. 32.

IV.—LEAVES LARGE, LANCEOLATE, OVATE-LANCEOLATE, OR OVATE.

(I.)—Leaves without a midrib on upper surface.

(a) Leaves with stomatic lines or bands.

12. *Cunninghamia.*—Leaves broad and decurrent at the base, the lower surface marked with two conspicuous stomatic bands. Plate 12, fig. 33.

11. *Araucaria.*—Section Colymbea. Leaves shortly stalked with inconspicuous stomatic lines on both surfaces. Plate 12, fig. 34.

(b) Leaves without visible stomatic lines.

10. *Agathis.*—Kauri Pines. Leaves with many parallel veins, between which the resin-canals are situated. Plate 12, fig. 35.

44. *Podocarpus Wallichianus* and *P. Nagi.*—Leaves with many parallel veins, beneath which the resin-canals are situated. Plate 12, fig. 36.

(II.)—Leaves with a prominent midrib on the upper surface.

44. *Podocarpus macrophyllus, P. neriifolius,* and *P. chilinus.*—Leaves without visible stomatic lines. Plate 12, fig. 37.

V.—BRANCHES BEARING CLADODES, *I.E.*, MODIFIED BRANCHLETS RESEMBLING TRUE LEAVES, THE LATTER BEING REDUCED TO SCALES.

47. *Phyllocladus.*—Cladodes flat, rhombic, arising each out of the axil of a scale. Plate 13, fig. 38.

20. *Sciadopitys.*—Umbrella Pine. Cladodes long, rigid, somewhat resembling pine-needles, furrowed above and grooved beneath, in whorls at the apices of the branchlets; scales spirally arranged on the internodes. Plate 13, fig. 39.

II.—LEAVES ARRANGED IN OPPOSITE DECUSSATE PAIRS, SCALE-LIKE.

A.—BRANCHLET-SYSTEMS FLATTENED, ALL THE BRANCHLETS ARISING FROM THE MAIN AXIS IN ONE PLANE.

21. *Cupressus,* in part.—Plate 13, fig. 40.

22. *Thuya.*—Plate 13, fig. 41.

23. *Biota.*—Plate 13, fig. 42.

24. *Microbiota.*—Plate 13, fig. 43.

27. *Thujopsis.*—Plate 13, fig. 44.

25. *Libocedrus,* in part.—Plate 13, fig. 45.

26. *Fokienia.*—Plate 13, fig. 46.

These genera cannot be individually distinguished by the foliage alone. See special key.

B.—BRANCHLET-SYSTEMS NOT FLATTENED, THE BRANCHLETS ARISING AT VARYING ANGLES AND SPREADING RADIALLY FROM THE MAIN AXIS.

I.—LEAVES GLANDULAR OR WITH A MEDIAN FURROW ON THE DORSAL SURFACE.

21. *Cupressus,* in part.—See special key. Plate 13, fig. 47.

II.—LEAVES NON-GLANDULAR, AND WITHOUT A DORSAL FURROW.

33. *Widdringtonia.* — Leaves rhombic or hexagonal, non-imbricate, in opposite decussate pairs on the ultimate branchlets, spirally arranged on the main axes of the branchlets. Plate 13, fig. 48.

46. *Microcachrys.*—Leaves ovate, densely imbricate, with a rounded apex. Plate 14, fig. 49.

30. *Diselma.*—Leaves rhombic, densely imbricate, tapering to an acute apex. Plate 14, fig. 50.

III.—LEAVES WITH A STRONG PECULIAR ODOUR, ACICULAR FOLIAGE OCCURRING ON OCCASIONAL BRANCHES OF THE TREES IN MOST SPECIES.

28. *Juniperus.*—Section *Sabina,* in part. See special key. Plate 14, fig. 51.

IV.—LEAVES WITH TWO LATERAL FURROWS ON THE DORSAL SURFACE.

27. *Libocedrus Bidwillii* and *L. tetragona.* — See special key. Plate 14, fig. 52.

III.—LEAVES IN WHORLS OF THREES.

A.—LEAVES SPATULATE OR ACICULAR, SPREADING.

29. *Fitzroya.*—Leaves decurrent on the branchlet, spatulate, rounded and incurved at the apex; upper surface concave, with two longitudinal stomatic hollows; lower surface convex, with stomatic hollows. Plate 14, fig. 53.

28. *Juniperus.*—Sections *Oxycedrus, Caryocedrus,* and, in part, *Sabina* (two species). Leaves with a strong peculiar odour, acicular. See special key. Plate 14, fig. 54.

B.—LEAVES SCALE-LIKE, DECURRENT, COVERING ENTIRELY THE AXIS OF THE TWIG.

31. *Callitris.* — Leaves decurrent for their whole length, except the free triangular tip. Ultimate branchlets tereté or trigonous. Plate 14, fig. 55.

32. *Actinostrobus.* — Leaves decurrent for half their length; free part triangular. Ultimate branchlets trigonous. Plate 14, fig. 56.

IV.—LEAVES IN WHORLS OF FOURS.

34. *Tetraclinis.*—Leaves scale-like, decurrent, the lateral pair slightly larger than and partly covering the facial pair. Ultimate branchlets flattened. Plate 14, fig. 57.

35. *Callitropsis.*—Leaves broad at the base, and gradually narrowing towards the apex; trigonous. Ultimate branchlets terete. Plate 14, fig. 58.

DESCRIPTION OF GENERA AND SPECIES.

ABIETINEAE.

1.—*PICEA.* SPRUCES.

Large trees in their native countries, yielding timber known commercially as "White Deal." *Twigs* bearing peg-like projections from which the leaves arise singly. *Leaves* spirally arranged, needle-like, either four-angled or flattened in cross-section, persisting for several years. *Cones* pendulous, with persistent woody scales, ripening in the first autumn. *Seeds* small, with a large, easily detachable wing.

Thirty-eight species have been described, about twenty-seven of which are in cultivation. Of these, only two, *P. excelsa* and *P. sitchensis*, are profitable forest-trees in the British Isles. The remaining species are only planted for ornament. *Distribution*; temperate regions of the northern hemisphere; Europe, Asia Minor, Caucasus, Siberia, China, Japan, Himalayas, and North America.

Spruce grows well in most soils and produces a large volume of timber in mountainous districts on land too poor for any other crop. It may be grown in mixture with larch or other species, but does best when planted pure. It is very free from disease and stands wind well. See Nos. 3 and 19.

The genus is marked into three natural sections by the shape of the leaves and the distribution of the stomatic bands thereon.

I.—OMORICA—FLAT-LEAVED SPRUCES.

Leaves with two surfaces, flattened from above downwards; two white stomatic bands present on the dorsal surface, which is directed towards the ground; ventral surface green and without stomatic lines.

A.—Twigs glabrous.

1. *P. jezoensis*, Carrière. (*P. hondoensis*, Mayr., *P. ajanensis*, Fischer.)—Manchuria, Japan. Twigs buff-coloured in first winter. Buds slightly resinous. Leaves in a pectinate arrangement, slightly convex on both surfaces, thin, blunt, or ending in a short point. Up to 150 feet high. Cultivated for ornament.

2. *P. brachytila*, Pritzel.—Central China. Twigs buff-coloured in the first winter. Leaves in a pectinate arrangement, broad-keeled on both surfaces, ending in a sharp cartilaginous point. Up to 80 feet high. Cultivated for ornament.

3. *P. sitchensis*, Trautvetter and Meyer. — Sitka Spruce. West coast of North America from Alaska to California. Twigs yellow in the first winter. Leaves in a pectinate arrangement, narrow, convex on dorsal white surface, angled on ventral green surface, ending in a needle-like point. Up to 180 feet high. Invaluable for commercial planting in the British Isles, where it is

extremely vigorous, thriving on wet ground, in acid peaty soil, and in exposed situations. The timber is the most valuable of all spruce woods.

4. *P. spinulosa,* Beissner. (*P. morindoides,* Rehder). — Sikkim Spruce, Eastern Himalayas. Twigs buff-coloured in the first winter. Leaves spreading radially on the pendulous branchlets; long, narrow, prominently keeled on both surfaces, ending in a sharp point. Plate 9, fig. 4. Up to 200 feet. Cultivated for ornament.

B.—Twigs pubescent.

5. *P. Breweriana,* Watson. — Brewer's Spruce. Oregon and California. Leaves spreading radially on the pendulous branchlets, convex on both surfaces, and ending in a short point. Up to 150 feet high. Cultivated for ornament.

6. *P. Omorika,* Bolle.—Servian Spruce. Drina Valley in Servia and Bosnia. Leaves in a pectinate arrangement, thin, keeled on both surfaces, ending in a short point. Up to 100 feet high. Cultivated for ornament.

II.—BICOLOR—INTERMEDIATE SPRUCES.

Leaves four-sided and four-angled; stomatic lines on the two dorsal sides broad and conspicuous, on the two ventral sides narrow and indistinct.

7. *P. bicolor,* Mayr. — Alcock's Spruce. Japan. Twigs reddish brown in first winter, glabrous on lateral branchlets, usually pubescent in the furrows on leading shoots of branches or trees. Leaves stout, rigid, ending in a short point. Buds conical. Up to 80 feet high. Cultivated for ornament.

8. *P. likiangensis,* Pritzel.—Likiang Spruce. S.W. China. Twigs glabrous, occasionally with sparse hairs, pale brown in first winter. Buds conical, covered with white resin. Leaves long, slender, ending in a sharp cartilaginous point. Up to 100 feet high. Cultivated for ornament.

9. *P. Balfouriana,* Rehder and Wilson. — China. Twigs pubescent, pale brown in first winter. Buds conical. Leaves with a bluish tinge, short, ending in a short point; stomatic lines on ventral green sides clearly discernible with a lens. Up to 100 feet high. Cultivated for ornament.

10. *P. purpurea,* Masters. — China. Twigs pubescent, pale brown in first winter. Buds conical. Leaves short and short-pointed, stomatic lines on ventral green sides barely discernible with a lens. Up to 100 feet high. Cultivated for ornament.

III.—MORINDA—SQUARE-LEAVED SPRUCES.

Leaves four-sided and four-angled; stomatic lines similar on all four sides, and not forming broad bands.

A.—Leaves on lateral branchlets radially arranged, spreading uniformly on all sides; twigs quite glabrous.

11. *P. Morinda,* Link. (*P. Smithiana,* Boissier).—West Himalayan Spruce. W. Himalayas. Branchlets pendulous, twigs grey in first winter. Buds large,

ovoid, slightly resinous. Leaves long and drooping. Up to 200 feet high. Cultivated for ornament.

12. *P. Maximowiczii,* Regel.—Japan. Branchlets not pendulous, twigs light brown in first winter. Buds ovoid, covered with white resin. Leaves short, ending in a sharp cartilaginous point. Up to 50 feet high. Rare in cultivation.

B.—Leaves on lateral branches in an imperfect pectinate arrangement, not pectinate in two sets on the lower sides of the branchlets.

(I).—Twigs quite glabrous.

13. *P. Schrenkiana,* Fischer and Meyer.—Central Asia. Twigs ashy grey in first winter. Terminal buds sub-globose, with outer scales pubescent. Leaves up to 1¼ in. long, rigid, ending in a sharp point. Up to 100 feet high. Cultivated for ornament.

14. *P. pungens,* Engelmann.—Blue Spruce. North America. Twigs reddish brown in first winter. Buds large, with the tips of the outer scales usually loose and reflexed. Leaves up to 1¼ in. long, stout, rigid, with a short hard point. Up to 100 feet high. Cultivated for ornament.

15. *P. polita,* Carrière.—Japan. Twigs red in first winter. Buds large, ovoid, shining reddish brown, with closely imbricated scales. Leaves up to 1¼ in. long, stout, rigid, curved, ending in a spine-like point; shining green in colour. Up to 130 feet high. Cultivated for ornament.

16. *P. asperata,* Masters.—W. China. Twigs shining yellowish brown in first winter. Buds conical. Leaves up to ¾ in. long, stiff, with a needle-like point. Up to 100 feet high. Cultivated for ornament.

(II).—Twigs glabrous or slightly pubescent.

17. *P. albertiana,* Stewardson Brown.—Western N. America. Twigs greyish yellow in first winter; glabrous or with minute hairs on the pegs, from which the leaves arise. Buds ovoid, slightly resinous, the terminal bud girt with a ring of long pointed scales. Leaves 1 in. long, ending in a short blunt point. Up to 160 feet high. Cultivated for ornament.

C.—Leaves on lateral branches imbricated on the upper side of the branchlets; those below pectinate and spreading laterally in two sets.

(I).—Twigs glabrous.

18. *P. alba,* Link.—White Spruce. North America. Twigs glaucous, greyish or pale brown in first winter. Buds brown, with bifid, non-ciliate scales. Leaves short (½ in.), ending in a short hard point, emitting a disagreeable odour when bruised. Up to 100 feet high. Of little value as a

forest-tree in the British Isles. It is absolutely hardy, and is useful for shelter belts at high elevations.

19. *P. excelsa,* Link. — Common Spruce. Central and Northern Europe. Twigs red in first winter, usually quite glabrous. Terminal buds conical, acute, non-resinous. Leaves about ¾ in. long, short-pointed or blunt. Up to 150 feet high. An important forest-tree of N. Europe, large quantities of the timber, called white deal, being imported into England. Valuable for commercial planting in the British Isles, where it thrives on poor shallow soil.

20. *P. Wilsoni,* Masters.—China. Twigs pale yellow. Buds ovoid, with brown scales. Leaves slender, up to 1 in. long, curved, dark shining green; stomatic lines inconspicuous. Up to 40 feet high. Rare in cultivation.

(II).—Twigs either glabrous or sparsely hairy.

21. *P. Koyamai,* Shirasawa. — Japan. Twigs orange, glabrous, or with sparse hairs in the furrows, slightly glaucous. Buds ovoid, pointed, shining brown, surrounded by a ring of pointed scales. Leaves short (½ in.), stout, acute at apex. Up to 60 feet. Rare in cultivation.

21A. *P. excelsa,* var. *alpestris.*—A rare tree in the European Alps. Twigs variable in pubescence, usually with some short hairs, otherwise as in the type.

(III).—Twigs plainly pubescent.

(*a*) *Terminal bud girt with a ring of thread-like outer scales, equalling or exceeding the bud in length.*

22. *P. nigra,* Link.—Black Spruce. North America. Twigs yellowish brown, covered with a dense, short, glandular pubescence. Leaves short (½ in.), bluish or glaucous green. Up to 70 feet high. Cultivated for ornament.

23. *P. rubra,* Link.—Red Spruce. North America. Twigs yellowish brown, covered with a dense, short, glandular pubescence. Leaves short (½ in.), curved, yellowish or dark green, not glaucous. Up to 80 feet high. Rare in cultivation.

24. *P. Glehnii,* Masters.—Asia Minor. Twigs reddish brown, with short non-glandular pubescence, confined to the furrows between the pulvini. Leaves slender, short (½ in.), ending in a short point. Up to 100 feet high. Cultivated for ornament.

(*b*) *Terminal bud without a ring of thread-like scales.*

25. *P. orientalis,* Carrière. — Oriental Spruce. Caucasus and Asia Minor. Twigs slender, brown in the first winter, covered with a dense, short, non-glandular pubescence. Leaves less than ½ in. long, shining dark green, blunt and levelled at the tip. Up to 180 feet. Cultivated for ornament.

26. *P. Engelmanni,* Engelmann. — North America. Twigs greyish yellow, with sparse minute glandular pubescence. Leaves bluish green, 1 in. long, blunt at the tip, emitting a disagreeable odour when bruised. Up to 150 feet high. Cultivated for ornament.

27. *P. obovata*, Ledebour.—Siberian Spruce. Scandinavia, Finland, Russia, and Siberia. Twigs reddish brown, covered with a dense, minute, non-glandular pubescence. Leaves similar to *P. excelsa*, up to $\frac{3}{5}$ in. long, blunt or short-pointed at the apex. Up to 200 feet high. Cultivated for ornament. The timber is known commercially as white deal, and large quantities are imported into the British Isles.

2.—*TSUGA*. HEMLOCK FIRS.

Usually large trees, yielding commercial timber. *Leaves* linear, spirally arranged, and either spreading radially, as in one species, or, in most cases, thrown into a pectinate arrangement. Petioles short, slender, arising from prominent leaf-bases, and appressed against the twigs. The leaf has a single resin-canal, lying in the middle line between the vascular bundle and the epidermis of the lower surface. *Cones* solitary, small, pendulous, with persistent woody scales and concealed bracts; ripening in the first autumn. Seeds, two on each scale, with resin-vesicles, winged.

There are nine species, of which only one, *T. albertiana*, is suitable for commercial planting in the British Isles. The remainder are cultivated for ornament. *Distribution*: temperate North America, Japan, China, and the Himalayas.

The genus is divided into two sections.

I.—HESPEROPEUCE, Engelmann.

Leaves radially arranged, branchlets spreading, and not in one plane.

1. *T. Pattoniana*, Sénéclauze.—Western N. America. Leaves $\frac{1}{2}$–$\frac{7}{8}$ in. long, rounded or keeled above, bearing stomatic lines on both surfaces. Leaves on the upper side of the branchlet curved and directed outwards and forwards. Up to 150 feet high. Cultivated for ornament.

2. *T. Jeffreyi*, Henry. — Leaves less than $\frac{1}{2}$ in. long, serrulate in margin; upper surface flattened and grooved, with 4–6 broken stomatic lines near the apex; lower surface convex, with stomatic lines the whole length of the leaf. Leaves directed outwards and not forwards. This is a hybrid, *T. Pattoniana* × *T. albertiana*, and is rare in cultivation.

II.—MICROPEUCE, Spach.

Leaves in a pectinate arrangement, branchlet systems flattened in one plane. Leaves flat, grooved above, bearing stomatic lines on the lower surface only.

A.—Leaves serrulate in margin. Twigs pubescent.

3. *T. canadensis*, Carrière.—Eastern Hemlock. Eastern N. America. Leaves $\frac{1}{3}$–$\frac{2}{3}$ in. long, usually tapering from the base to the acute or rounded apex; lower surface with two distinct narrow stomatic bands, separated from the margins by green bands. Buds brown, ovoid, pointed, composed of pubescent, keeled, acute scales. Up to 100 feet high. Common as an ornamental tree.

4. *T. albertiana,* Sénéclauze (*T. Mertensiana,* Lindley and Gordon).—Western Hemlock. Western N. America. Leaves ¼–¾ in. long, usually rounded at the apex, and uniform in breadth; lower surface with two ill-defined broad white stomatic bands, there being no distinct bands of green between them and the edges of the leaf. Buds greyish, ovoid, apex obtuse and flattened; scales keeled, pubescent. Plate 9, fig. 5. Up to 200 feet high. Common as an ornamental tree, and occasionally planted commercially. It grows well in most soils, except on chalk or stiff clay, and does best in a mild climate. It will not stand great exposure, but suffers less from wind than Douglas Fir. It bears great shade, and is useful for underplanting larch. The wood is about the same value as spruce.

5. *T. Brunoniana,* Carrière.—Himalayas. Leaves 1–1¼ in. long, gradually tapering from the base to the acute apex; lower surface silvery white, the stomatic bands well defined, and extending almost to the margins. Buds globose, flattened at the top, surrounded at the base by a ring of modified leafy scales; the outer scales, ovate, acute, pubescent. Up to 100 feet high. Cultivated in the milder parts of the British Isles as an ornamental tree.

6. *T. yunnanensis,* Masters.—China. Leaves ½–¾ in. long, rounded or acute at the apex; two conspicuous stomatic bands beneath. Up to 100 feet high. Rare in cultivation.

B.—Leaves entire in margin. Twigs glabrous.

7. *T. Sieboldii,* Carrière.—Japan. Leaves ¼–1 in. long, oblong, rounded and notched at the apex, shining above, lower surface with two narrow, well-defined white stomatic bands. Buds red, ovoid and slightly acute at the apex; scales glabrous and ciliate. Up to 100 feet high. Cultivated for ornament.

C.—Leaves entire in margin. Twigs pubescent.

8. *T. diversifolia,* Maximowicz.—Japan. Twigs pubescent both on the leaf bases and in the furrows between them. Leaves ¼–½ in. long, oblong, rounded and notched at the apex; lower surface with two narrow, well-defined white stomatic bands. Buds red, pyriform, flattened above; scales obtuse, minutely pubescent. Up to 80 feet high. Rare in cultivation.

9. *T. caroliniana,* Engelmann.—Southern United States. Twigs pubescent in the furrows between the leaf bases, which are glabrous. Leaves ¼–¾ in. long, oblong, rounded at the apex, which is entire, minutely notched or mucronate; lower surface with two narrow, well-defined stomatic bands. Buds reddish, ovoid, sharp-pointed; scales indistinctly keeled. Up to 60 feet high. Rare in cultivation.

10. *T. chinensis,* Pritzel.—China. Twigs with a sparse pubescence. Leaves up to 1 in. long, rounded and minutely notched at the apex, with indistinct stomatic lines on the lower surface. Buds globose. Up to 100 feet high. Rare in cultivation.

3.—*PSEUDOTSUGA.* DOUGLAS FIRS.

Large trees, yielding commercial timber of excellent quality. *Twigs* with raised, coloured, slightly prominent bases, from which the leaves arise. *Leaves* linear, narrowed at the base, upper surface furrowed, lower surface with two bands of stomata; resin-canals, two, marginal. *Buds* spindle-shaped, sharp-pointed, with shining brown scales. *Cones* pendulous, with persistent woody scales and protruding trident-like bracts; ripening in the first autumn. Seeds dark shining reddish brown above, light brown mottled with white beneath; wing not detachable, rounded at the summit.

There are seven species, of which only one, *P. Douglasii*, is suitable for commercial planting in the British Isles. Most of the other species are in cultivation as ornamental trees. *Distribution*: Western N. America, West China, Japan, and Formosa.

I.—AMERICANAE. LEAVES UNDIVIDED AT THE APEX.

1. *P. Douglasii*, Carrière.—Oregon Douglas Fir. Pacific coast region of N. America. Branchlets pubescent. Leaves thin, flat beneath, 1–1¼ in. long, with fragrant pine-apple odour, readily perceptible when bruised. Cones 3–4 in. long, with straight, erect bracts. Plate 9, fig. 3; Plate 15, fig. 72A. An important forest tree in its native country, attaining 300 feet in height, and one of the most valuable species introduced into Great Britain and Ireland, where it produces a large volume of excellent timber in a short term of years. It thrives on any soil, provided it is moist and well drained, and does not contain more than about 2 per cent. of lime. It may be planted in mixture with larch or *Thuya plicata*, but succeeds best when planted pure. It cleans its stem with great difficulty, and even when spaced 4 feet apart may require artificial pruning. It suffers from frost in the young stage, and does not thrive in situations exposed to the wind. The timber is strong and durable, resembling larch in appearance, and is used for the same purposes.

1A. Var. *caesia*, Schwerin.—Northern Rocky Mountains. This differs from the type in the glabrous branchlets, thicker needles, and smaller cones, 2½ in. long. Up to 150 feet high. Rare in cultivation.

2. *P. glauca*, Mayr.—Colorado Douglas Fir. Rocky Mountains, Colorado to Mexico. Branchlets variable in pubescence, often glaucous. Leaves thick, rounded beneath, 1–1¼ in. long, with strong turpentine odour. Cones 2–3 in. long, with reflexed bracts. Plate 15, fig. 72B. Up to 90 feet high. In cultivation, but only as an ornamental tree.

3. *P. macrocarpa*, Mayr.—Southern California. Branchlets variable in pubescence. Leaves thin, flat beneath, with recurved margins, 1–1¾ in. long, ending in a cartilaginous point. Cones very large, 3½–7 in. long, with straight erect bracts. Up to 80 feet high. Rare in cultivation.

II.—ASIATICAE. LEAVES BIFID AT THE APEX.

A.—Branchlets glabrous.

4. *P. japonica,* Beissner. — Japan. Leaves about 1 in. long, thin, not glaucous. Cones small, about 1½ in. long, with short, reflexed bracts. Up to 100 feet high. Rare in cultivation.

B.—Branchlets pubescent.

5. *P. sinensis,* Dode. — North Yunnan, China. Leaves 1¼ in. long, with recurved margins. Cones 2 in. long, with short reflexed bracts. A large tree. Rare in cultivation.

6. *P. Forrestii,* Craib.—West Yunnan, China. Leaves nearly 2 in. long, with recurved margins. Cones 2¼ in. long, with long reflexed bracts. Up to 80 feet high. Rare in cultivation.

7. *P. Wilsoniana,* Hayata.—Formosa. Leaves ¾ in. long. Cones 2–2½ in. long, with short reflexed bracts. This species is possibly identical with *P. sinensis,* Dode, and is not yet introduced into cultivation.

4.—*ABIES.* SILVER FIRS.

Usually large trees, yielding commercial timber. *Twigs* woody in the second year, with circular scars left on the older branchlets after the fall of the leaves. *Leaves* evergreen, spirally arranged; linear, flattened, and thin in most species, quadrangular in cross-section in a few species; upper surface green, convex, with or without a median groove, occasionally with stomatic lines; lower surface with two broad stomatic bands, one on each side of the raised green midrib; sessile, but usually narrowed just above the expanded circular base; apex bifid or entire. Resin-canals, two, lateral, constant in position for each species in the leaves on sterile branches of adult trees, either median, when situated in the substance of the leaf, or marginal, when placed close to the epidermis. Their position in the leaves of young plants occasionally differs from that of adult trees of the same species, and consequently this is not always a reliable character. Plate 15, fig. 69. *Buds* with numerous imbricated scales, with or without resin, usually two to five at the ends of the branchlets. *Cones* erect on the branches, with closely imbricated, fan-shaped, woody scales, and hidden or projecting bracts, ripening and falling to pieces in the first autumn. *Seeds,* two on each scale, with resin-vesicles and with wings attached to the seeds.

There are about forty species, of which only three, *A. pectinata, A. grandis,* and *A. nobilis,* are suitable for commercial planting in the British Isles. About thirty-four of the remaining species are in cultivation as ornamental trees. *Distribution*: Europe, North America, Asia Minor, Caucasus, Siberia, Himalayas, China, Japan, and North Africa.

Silver firs grow well on any moist soil. Woods may be pure or a mixture with other species. They are intense shade-bearers, and are useful for under-

planting. They stand wind well, and in mixture with beech are excellent for shelter belts. They usually suffer greatly from attacks by Chermes (*Dreyfusia nusslini*), and are liable to injury by spring frost in the young stage. The timber is superior to ordinary white deal, which it resembles, and is mostly used locally, and not imported into Great Britain and Ireland. See Nos. 11, 21, and 23.

I.—LEAVES NOT BIFID. APEX SINGLE POINTED.

A.—Leaves radially arranged on the branchlets.

1. *A. Pinsapo,* Boissier.—Spanish Fir. Spain. Leaves rigid, short, less than ¾ inch in length, thick, acute at the apex, resin-canals median. Twigs glabrous. Buds resinous. Up to 100 feet high. Cultivated for ornament.

2. *A. cephalonica,* Loudon.—Grecian Fir. Greece. Leaves thin, flattened, about 1 in. long, ending in a sharp cartilaginous point; resin-canals marginal. Twigs glabrous. Buds resinous. In var. *Apollinis* the radial arrangement is imperfect, and the leaves end in a short point. Up to 100 feet high. Cultivated for ornament.

B.—Leaves on the lateral branches pectinate in arrangement, the two lateral sets in one plane.

3. *A. bracteata,* Nuttall.—Santa Lucia Fir. California. Leaves long, two inches or more, rigid, ending in a spine-like point; resin-canals marginal. Twigs glabrous, smooth. Buds elongated, fusiform, non-resinous. Up to 150 feet high. cultivated for ornament.

C.—Leaves irregularly arranged, those on the lower side of the branchlet not truly pectinate.

4. *A. concolor,* Lindley and Gordon.—Colorado White Fir. North America. Leaves imperfectly pectinate both above and below, some in the middle line being also directed forwards and not laterally outwards; up to 3 in. long; upper surface convex and not grooved, bearing 15–16 stomatic lines; resin-canals marginal. Twigs smooth, olive green, glabrous. Buds large, conical, resinous. Up to 150 feet high. Cultivated for ornament.

5. *A. lasiocarpa,* Nuttall.—Western N. America. Leaves sometimes assurgent above, 1½ in. long, narrow, with conspicuous stomatic lines on the upper surface, especially the anterior half. Resin-canals median. Twigs smooth, with a moderately dense, short, wavy pubescence. Buds small, conical, resinous. Up to 120 feet high. Cultivated for ornament.

6. *A. recurvata,* Masters.—China. Leaves sometimes assurgent, or strongly reflexed. Leaves rigid, sharp pointed, upper surface shining green, grooved; two inconspicuous stomatic bands on the lower surface; resin-canals marginal. Twigs smooth, shining yellowish grey, glabrous. Buds large, ovoid, with the tips of the scales projecting, covered with white resin. Up to 120 feet high. Rare in cultivation.

7. *A. holophylla,* Maximowicz.—Manchurian Fir. Manchuria. Leaves 1½ in. long, shining green above, greenish beneath, the two stomatic bands being inconspicuous to the unaided eye, though plainly visible with a lens. Twigs furrowed, sometimes smooth, glabrous, reddish brown. Buds small, globose, resinous. Up to 150 feet high. Rare in cultivation.

8. *A. squamata,* Masters.—China. Leaves sometimes assurgent above, up to 1 in. long, two broad stomatic bands below; scattered lines of stomata on upper surface near apex. Twigs shining red in first year, glabrous, rough, but not furrowed. Buds red, globose, resinous. Up to 120 feet. Rare in cultivation.

D.—Leaves on lateral branches not pectinate above, but densely crowded, those in the middle line directed forwards in imbricated ranks, their bases not being appressed to the twig. On the lower side of the branchlet the leaves are in two lateral sets.

9. *A. religiosa,* Schlechtendal.—Mexican Sacred Fir. Mexico. Leaves about 1 in. long, gradually narrowing from the middle to the usually entire apex; resin-canals marginal. Twigs with prominent pulvini and deep grooves and a dense, erect, minute pubescence. Buds shortly cylindrical, resinous. Up to 150 feet high. Rare in cultivation.

10. *A. sibirica,* Ledebour.—Siberian Fir. Russia and Siberia. Leaves long, up to 2½ in., and slender, uniform in width, with 4 or 5 lines in each stomatic band beneath, resin-canals median. Twigs ashy grey, smooth, with a scattered pubescence. Buds small, globose, resinous. Up to 100 feet high. Rare in cultivation.

E.—Leaves on lateral branches not pectinate above, those on the middle line covering the branchlet and curving upwards after being appressed to the twig for some distance at their base. The leaves on the lower side are in two lateral sets.

11. *A. nobilis,* Lindley.—Noble Fir. Western N. America. Leaves closely appressed to the twig, which they completely conceal, about 1 in. long, flattened, grooved on the upper surface; stomatic lines on both surfaces; resin-canals marginal. Twigs with a dense brown pubescence. Terminal buds surrounded with a ring of acute-pointed or thread-like pubescent scales. A valuable timber tree in its native country, where it attains a height of 240 feet, and important for planting at high elevations in the British Isles. It suffers from Chermes, and does not succeed at low altitudes.

12. *A. magnifica,* Murray.—Californian Red Fir. Western N. America. Leaves appressed to the twig for a short distance only, longer than in *A. nobilis,* and not grooved on the upper surface; stomatic lines on both surfaces; resin-canals marginal. Twigs and buds as in *A. nobilis.* Up to 200 feet high. Cultivated for ornament.

II.—LEAVES BIFID AT THE APEX.

A.—Leaves on lateral branches pectinate in arrangement; the two lateral sets either in one plane, or with their upper ranks directed upwards as well as outwards, showing a V-shaped depression between the two sets.

(I).—Twigs distinctly grooved.

13. *A. firma,* Siebold and Zuccarini.—Japanese Fir. Japan. Leaves in a V-shaped arrangement, rigid, very coriaceous, broad, up to 1½ in. long; resin-canals marginal. Twigs pubescent in the furrows between the slightly raised pulvini. Buds small, ovoid, only slightly resinous. Up to 150 feet high. Cultivated for ornament.

14. *A. Beissneriana,* Rehder and Wilson.—China. Leaves long, very broad, greyish beneath. Twigs grey, with a sparse pubescence in the grooves. Buds covered with white resin. Up to 200 feet high. Rare in cultivation.

15. *A. densa,* Griffith (*A. Webbiana,* Lindley).—Eastern Himalayan Fir. E. Himalayas. Leaves in a V-shaped arrangement, sometimes 2½ in. long; resin-canals marginal. Twigs with prominent pulvini and deep grooves, with a red pubescence confined to the grooves. Buds large, globose, resinous. Up to 200 feet high. Cultivated for ornament.

16. *A. brevifolia,* A. Henry (*A. Webbiana,* var. *brevifolia* A. Henry. *A. spectabilis,* var. *brevifolia,* Rehder).—Western Himalayan Fir. W. Himalayas. Leaves in a V-shaped arrangement, up to 1 in. long, greyish beneath, broken lines of stomata on upper surface near apex. Twigs grey, furrowed, with a red pubescence in the furrows. Buds globose, resinous. Up to 200 feet high. Rare in cultivation.

17. *A. brachyphylla,* Maximowicz (*A. umbellata,* Wilson).—Japan. Leaves in a V-shaped arrangement, short, scarcely 1 in. long; resin-canals median. Twigs glabrous, with prominent pulvini and deep grooves. Buds conical, resinous. Up to 100 feet high. Cultivated for ornament.

(II).—Twigs not distinctly grooved.

(a) Twigs glabrous.

18. *A. chensiensis,* Van Tieghem.—China. Leaves all in one plane, those in the upper rank about half the length of those below; up to 2 in. long. Twigs brown, glabrous. Buds slightly resinous, with prominent scales. Up to 120 feet high. Rare in cultivation.

19. *A. Delavayi,* Franchet.—China. Leaves dark green above, the two white bands beneath separated by a prominent green midrib, equalling in breadth the two marginal green bands; leaves broadest at the apex; margins sometimes incurved, or become so on drying; resin-canals marginal. Twigs light brown, slightly grooved, glabrous. Buds large, globose, purple, resinous. Up to 100 feet high. Rare in cultivation.

20. *A. Fargesii,* Franchet.—China. Leaves broad, only slightly bifid, very white beneath. Twigs brilliant red, minutely papillate, slightly furrowed, usually glabrous, but sometimes pubescent. Buds large, globose, covered with white resin. Up to 100 feet high. Rare in cultivation.

(*b*) *Twigs pubescent.*

21. *A. grandis,* Lindley.—Giant Fir. Western N. America. Leaves all in one plane, those in the upper rank about half the length of those below; up to 2 in. long; resin-canals marginal. Twigs olive green, minutely pubescent. Buds small, resinous. Plate 9, fig. 1; Plate 15, fig. 69 A. This is the fastest in growth of all the silver firs, and is important for commercial planting in the British Isles. It does not suffer as yet from Chermes, and is not liable to injury from frost in the young stage.

21 A. *A. Fargesii,* Franchet.—Twigs sometimes pubescent. See No. 20.

22. *A. Faxoniana,* Redher and Wilson.—China. Leaves pectinate, sometimes in a V-shaped arrangement, tapering from the middle to the apex, and ending in two sharp points. Twigs brown, slightly grooved, pubescent. Buds red, globose, resinous. Up to 100 feet high. Cultivated for ornament.

23. *A. pectinata,* De Candolle.—Common Silver Fir. Europe. Leaves pectinate in one plane, or tending to a V-shaped arrangement, about 1 in. long; resin-canals marginal. Twigs grey, with a short pubescence. Buds small, ovoid, non-resinous. A valuable forest tree in Central Europe, and important for commercial planting in the British Isles, where it produces a large volume of timber. It is liable to damage by spring frost, and may require the protection of nurses in its early stage, especially where there is a strong growth of grass. It suffers from Chermes, and is consequently difficult to establish.

24. *A. balsamea,* Miller.—Balsam Fir. East of N. America. Leaves slender, scarcely 1 in. long, two or three broken stomatic lines on the upper surface near the apex, and six to eight lines in each band on the lower surface; resin-canals median. Twigs smooth, grey, with scattered, short, erect pubescence. Buds globose, resinous. Plate 15, fig. 69 B. Up to 60 feet high. Cultivated for ornament.

25. *A. nephrolepis,* Maximowicz.—Manchuria. Leaves slender, up to 1¼ in. long, no stomatic lines above, two narrow bands beneath; resin-canals median. Twigs and buds as in *A. balsamea.* Up to 70 feet high. Rare in cultivation.

26. *A. Lowiana,* Murray. — Low's White Fir. California. Leaves in a V-shaped arrangement, 1½–2½ in. long, upper surface grooved, and with eight lines of stomata; resin-canals marginal. Twigs olive green, and minutely pubescent. Buds small, resinous. Up to 250 feet high. Cultivated for ornament.

B.—Leaves on lateral branches not pectinate above, but densely crowded, those in the middle line directed forwards in imbricated ranks, their bases not being appressed to the twig; on the lower side of the branchlet the leaves are in two lateral sets.

27. *A. Nordmanniana,* Spach.—Caucasian Fir. Caucasus. Leaves up to 1¼ in. long, with a rounded apex; resin-canals marginal. Twigs smooth, with short, scattered, erect pubescence. Buds ovoid, brown, non-resinous. Up to 200 feet high. Usually cultivated for ornament.

28. *A. amabilis,* Forbes.—Red Silver Fir. Western N. America. Leaves in arrangement and size like those of *A. Nordmanniana,* but darker-shining green, and with a truncate apex; a fragrant odour when bruised; resin-canals marginal. Twigs smooth, with a short, wavy pubescence. Buds small, globose, resinous. Up to 250 feet high. Cultivated for ornament.

29. *A. Mariesii,* Masters.—Maries' Fir. Japan. Leaves short and broad, with a rounded apex; resin-canals marginal. Twigs smooth, densely covered with a ferruginous pubescence. Buds small, globose, resinous. Up to 80 feet high. Cultivated for ornament.

30. *A. Veitchii,* Lindley.—Veitch's Silver Fir. Japan. Leaves up to 1 in. long, truncate at the apex, uniform in width, very white beneath, with 9 or 10 lines in each stomatic band; resin-canals median. Twigs smooth, covered with a dense, short, erect pubescence. Buds small, globose, purplish, resinous. Up to 70 feet high. Cultivated for ornament.

31. *A. sachalinensis,* Masters.—Kurile Islands. Leaves long, up to 1¾ in., and slender, uniform in width, with a rounded apex; lower surface with 7 or 8 lines in each stomatic band; resin-canals median. Twigs with prominent pulvini and deep grooves, and a dense short pubescence confined to the grooves. Buds small, globose, resinous. Up to 130 feet high. Cultivated for ornament.

32. *A. cilicica,* Carrière. Cilician Fir. Asia Minor. Leaves slender, up to 1¼ in. long, not conspicuously white beneath; resin-canals marginal. Twigs smooth, with scattered, short, erect pubescence. Buds small, ovoid, non-resinous, the scales keeled, and free at the tips. Up to 100 feet high. Cultivated for ornament.

C.—Leaves on lateral branches not truly pectinate but assurgent, that is, nearly all are directed vertically.

33. *A. numidica,* De Lannoy.—Algerian Fir. Algeria. Leaves sometimes pectinate above with a V-shaped depression between the two sets, but usually assurgent with the median leaves directed slightly backwards. Leaves short, broad, rounded at the tip; in most cases with 4–6 broken stomatic lines on the upper surface near the apex; resin-canals marginal. Twigs brown, glabrous,

with slightly raised pulvini. Buds large, ovoid, non-resinous. Up to 70 feet high. Cultivated for ornament.

34. *A. Forrestii,* Craib.—China. Leaves usually assurgent, but on weak branches, sometimes forming a narrow V above; lower surface very white; apex rounded. Twigs red in first winter, glabrous, minutely papillate, slightly grooved. Buds large, globose, covered with white resin. Up to 60 feet high. Cultivated for ornament.

35. *A. Fraseri,* Poiret.—Southern Balsam Fir. Alleghany Mountains, N. America. Leaves rarely more than ¾ in. long; resin-canals median. Twigs smooth, yellow, with a dense red curved or twisted pubescence. Buds globose, resinous. Up to 70 feet high. Cultivated for ornament.

36. *A. koreana,* Wilson.—Korea. Twigs greyish, slightly grooved, with minute hairs in the grooves. Leaves about ¾ in. long, broadest near the apex. Buds small, globose, resinous. Up to 60 feet high. Rare in cultivation.

D.—Leaves irregularly arranged, all directed more or less forwards; those above imperfectly covering the branchlet, those below mostly pectinate, but with some directed downwards and forwards.

37. *A. Pindrow,* Spach.—West Himalayan Fir. Western Himalayas. Leaves soft, pale green, up to 2½ in. long, with two sharp points at the apex; resin-canals marginal. Twigs smooth, greyish green, glabrous. Buds large, globose, resinous. Up to 200 feet high. Cultivated for ornament.

The following species, of which we have seen no cultivated specimens, may be mentioned:—

38. *A. marocanna,* Trabut.—Morocco. Said to be intermediate in foliage between *A. numidica* and *A. Pinsapo.*

39. *A. nebrodensis,* Mattei.—Sicily. A very rare species, occurring on the Sierra dei Pine, near Polizzi, in Sicily; only one tree known. It is intermediate in foliage between *A. pectinata* and *A. cephalonica.*

40. *A. Vilmoriniana,* Masters.—This is a hybrid between *A. Pinsapo* and *A. cephalonica.*

5.—*KETELEERIA.*

Usually large trees. *Leaves* solitary, spirally arranged, usually thrown into a pectinate arrangement on lateral branches; linear, with a narrow stalk-like base expanded into a circular disc; apex acuminate and spine-tipped on young plants, rounded and slightly notched on adult trees; upper surface with a mid-rib prominent in a broad longitudinal depression; lower surface with two white stomatic bands; vascular bundle undivided, with two resin-canals close to the epidermis of the lower surface near the outer angles. *Twigs* smooth, with circular depressions, from which the leaves arise, and which remain as scars on the older branches after the fall of the leaves. *Buds* ovoid, with numerous

imbricated scales, which persist after the branchlet has developed as a conspicuous sheath at its base. *Cones* erect on the branches, with persistent woody scales and trident-like bracts, about half as long as the scales; ripening in the first year. Seeds with resin-vesicles and hatchet-shaped wings.

Three species are known, two of which have been introduced into Europe, but are still rare in cultivation. *Distribution*: China, Japan, and Tonking.

1. *K. Fortunei,* Carrière.—Foochow, Eastern China. Leaves with twelve to sixteen lines in each stomatic band. Twigs with a scattered short wavy pubescence. Up to 80 feet high.

2. *K. Davidiana,* Beissner.—China and Formosa. Leaves with nine lines in each stomatic band. Twigs with short, stiff, erect hairs. Plate 9, fig. 2. Up to 100 feet high.

3. *K. Evelyniana,* Masters. — China and Formosa. Possibly identical with *K. Davidiana,* which it resembles, differing mainly in the smaller cones.

6.—*CEDRUS.* CEDARS.

Large trees, with valuable wood. *Branchlets* of two kinds—(1) long shoots, bearing solitary leaves in spiral order; and (2) short shoots or spurs, with clusters of 30 or 40 leaves. *Leaves* evergreen, persisting three to six years; acicular, rigid, sharp-pointed, more or less triangular in section; with stomatic lines on all sides; fibro-vascular bundle undivided, two resin-canals close to the epidermis of the lower surface. *Buds* minute, ovoid, with a few brown scales, which persist after the opening of the bud. *Cones* erect on the branches, ellipsoidal or cylindrical, with woody scales, and very short bracts; ripening in three years, and falling in pieces when ripe. Seeds two on each scale, with large wings.

Four species have been described, each confined to a definite territory, and occurring in Syria, Cyprus, Himalaya, and the Atlas Mountains. They are extensively planted as ornamental trees, and thrive well in the British Isles. Cedars do best in a warm, deep, well-drained soil, in situations sheltered from the prevailing wind. The wood is oily, sweet-scented, with conspicuous resin-cells; heartwood yellowish brown, very durable. One of the most important timbers of north-western India and N. Africa. The "cedar" of commerce is usually the wood of *Cedrela odorata,* a tree found in the West Indies and Central America; or of *Juniperus virginiana,* when it is called "pencil cedar."

1. *C. Libani,* Barrelier (*C. libanotica,* Trew).—Lebanon Cedar. Mountains of Syria and Asia Minor. Leaves up to 1¼ in. long, broader than thick. Branchlets not pendulous, glabrous, or with slight short pubescence. Leading shoot of young tree erect, or slightly bent, not pendulous. Plate 2, fig. 9. Up to 100 feet high.

2. *C. Deodara,* Lawson.—Deodar. Himalaya. Leaves up to 2 in. long, as thick as broad. Branchlets always pendulous, grey, and densely pubescent. Leading shoot of young tree pendulous. Up to 200 feet high.

3. *C. brevifolia,* A. Henry.—Cyprus Cedar. Cyprus. Resembling *L. Libani* in characters of leading shoot and branchlets, but with very short leaves, not exceeding ½ in. in length. Up to 60 feet high.

4. *C. atlantica,* Manetti.—Atlas Cedar. Atlas Mountains of Morocco and Algeria. Leaves up to 1 in. long, usually as thick as, or thicker than, broad. Branchlets not pendulous, covered with a short, dense pubescence. Young trees stiffer in habit than the Lebanon Cedar, and with an erect leader.

7.—*LARIX.* LARCHES.

Usually tall trees, with valuable wood. *Twigs* woody in the second year, marked by the longitudinal cushion-like leaf-bases (pulvini) of the previous year. The marginal resin-canals of the pulvini in some species are large and conspicuous, showing as raised translucent edges. *Leaves* arranged in two ways: (1) those on the long shoots of the current season arising singly in spiral order; and (2) those at the summit of the short shoots or spurs, borne in clusters of 30–60; soft, deciduous, all falling in autumn, linear, thin, sessile; lower surface with a midrib and two stomatic bands; upper surface in some species with a midrib and indistinct stomatic bands; resin-canals, two, lateral. *Buds* globose, with short appressed scales. *Cones* erect on the branches; conical or ovoid, with persistent woody scales; ripening in the first autumn. Seeds, two on each scale, small, with a wing along the outer edge and at the apex.

There are about fifteen species, eleven of which are in cultivation. Of these, *L. europaea, L. leptolepis,* and *L. occidentalis,* and the hybrid L. *eurolepis* are suitable for commercial planting in the British Isles, where they are profitable forest trees if grown under suitable conditions. The remaining species are rarely successful in cultivation owing to their liability to spring frosts. See Nos. 1, 5, 8, 11. *Distribution*: cold regions of the northern hemisphere, i.e., plains near the Arctic Circle, and in the high mountains of the temperate zone in Asia, Europe, and North America.

Larch grows well on the sheltered slopes of hills, where the soil is porous and well-drained, and should be grown in mixture with beech or other species. It forms durable heartwood at an early age, and yields a profitable return from thinnings. The wood is brownish white, moderately hard and heavy, with resin-canals.

SPECIES IN CULTIVATION.

I.—TWIGS GLABROUS.

A.—Twigs without a waxy bloom.

1. *L. europaea,* De Candolle (*L. decidua,* Miller).—Common or European Larch. Central Europe, in Alps, Silesia, Carpathians, and Poland. Twigs yellow, pulvini without raised translucent edges. Buds golden brown, non-resinous, scales around terminal bud mucronate. Leaves up to 1¼ in. long, narrow; upper surface sometimes keeled, and with indistinct, broken stomatic

lines; lower surface keeled, with two stomatic bands; apex acute. Dried leafy branch without odour. Plate 9, fig. 7. Cones conical, scales straight or incurved, with slightly protruding bracts. A tree up to 150 feet, important for timber in the mountains of Central Europe. At one time it was extensively planted in Great Britain, but owing to attacks of Larch Canker Fungus (*Dasycypha calycina*) its cultivation is now restricted.

2. *L. sibirica,* Ledebour.—Siberian Larch. N. Russia and Siberia. Resembles *L. europaea.* Buds black, with a chequered appearance, due to the ciliated margins of the scales. Leaves 1–2 in. long, flattened; upper surface with two stomatic bands; lower surface deeply keeled, and with two stomatic bands; apex rounded. Leafy branch when dry emitting a strong peculiar odour. Cones conical, with fewer, larger scales than *L. europaea,* and concealed bracts. A tree, 100 feet, important in the forests of N. Russia. It is scarcely ever cultivated, as it suffers from spring frost in Great Britain.

3. *L. dahurica,* Turczaninow. — Dahurian Larch. Siberia and Korea. Resembles *L. europaea,* but may be distinguished by the conspicuous resin-canals of the pulvini visible as raised translucent edges. Leaves ½–1 in. long, flattened; lower surface keeled, with two stomatic bands; upper surface with indistinct broken stomatic lines; apex acute. Cones small, conical, with glabrous scales and concealed bracts. A tree, 80 feet. Rare in cultivation in the British Isles.

4. *L. Potanini,* Batalin.—China and Tibet. Twigs a brilliant orange colour. Leaves ¾–1⅛ in. long; upper surface prominently keeled, with indistinct broken stomatic lines; lower surface prominently keeled, with two stomatic bands; apex acuminate. Cones oblong or ovoid, up to 1¾ in. long, without stalks, apex blunt; scales numerous, rounded, each with a central notch; bracts usually protruding. A tree 70 feet high, in West China, where it is known as "Hung Sha," and valued for its timber. Rare in cultivation in the British Isles.

B.—Twigs with a waxy bloom.

5. *L. leptolepis,* Murray.—Japanese Larch. Japan. Twigs a brilliant red colour. Leaves up to 1½ in. long, glaucous; upper surface keeled, with broken stomatic lines; lower surface keeled, with two stomatic bands; apex acute. Cones globose, scales much reflected; bracts short, concealed. A tree up to 100 feet, important for timber in its native country. Extensively planted in the British Isles, where it is a valuable forest tree, yielding profitable thinnings at an early age. The timber is said to be inferior to European Larch. Owing to its vigorous growth it is not subject to Larch Canker.

6. *L. americana,* Michaux.—Tamarack. North America. Twigs glaucous in the first year, turning light brown in the second year. Leaves ½–1½ in. long, triangular in cross-section, narrow; lower surface with two stomatic bands; apex acute. Cones ovoid, small, composed of few rounded scales, with incurved

margins. A tree up to 80 feet in its native country, where it is valuable for timber. Cultivated in the British Isles, but has no value as a commercial tree.

II.—TWIGS WITH A SCATTERED PUBESCENCE.

A.—Twigs without a waxy bloom.

7. *L. Griffithii,* J. D. Hooker.—Sikkim Larch. Sikkim and Nepal. Twigs reddish-brown in colour, covered with short wavy hairs. Leaves 1–1¼ in. long; upper surface with broken stomatic lines; lower surface keeled, with two stomatic bands; apex acute. Cones cylindrical, 2–4 in. long; scales four-sided, furrowed, downy towards the base; bracts awl-shaped, protruding. A tree 60 feet high in its native country. Rare in cultivation in the British Isles.

8. *L. occidentalis,* Nuttall.—Western Larch. West N. America. Twigs reddish-brown in colour, covered with a minute pubescence. Leaves 1–2 in. long; upper surface convex, with stomatic lines; lower surface keeled, with two stomatic bands; apex acute. Cones ovoid, with the scales minutely pubescent and slightly reflexed; bracts protruding, reflexed. A tree up to 200 feet in its native country. It is in cultivation in the British Isles; but is inferior to Japanese or European larch for commercial planting.

9. *L. olgensis,* A. Henry.—Olga Bay Larch. Eastern Siberia. Twigs reddish-brown in colour, densely covered with long hairs; resin-canals in the pulvini visible as raised translucent edges. Leaves ½–¾ in. long; upper surface convex; lower surface keeled, with two stomatic bands. Cones small, ½–¾ in. long, with 20–30 scales, covered with a dense, short pubescence; bracts protruding. A small tree. Rare in cultivation.

B.—Twigs with a waxy bloom.

10. *L. kurilensis,* Mayr.—Kurile Larch. Kurile Islands and Saghalien. Twigs dark red or violet in colour, with appressed pulvini, having conspicuous translucent edges. Leaves ½–1 in. long; upper surface occasionally with broken stomatic lines; lower surface keeled, with two stomatic bands; apex acute. Cones small, ½–¾ in. long, with about 15 slightly pubescent scales. A tree up to 70 feet in its native country, with valuable timber. Rare in cultivation in the British Isles.

10 A. *L. leptolepis,* Murray.—Twigs brilliant red in colour, with long brown hairs, dense or scattered, or occasionally glabrous. See No. 5.

11. *L. eurolepis,* A. Henry.—Dunkeld (hybrid) Larch. Twigs yellow or pinkish in colour, with scattered hairs, sometimes glabrous. Leaves up to 1½ in. long, glaucous; upper surface with broken, indistinct stomatic lines; lower surface keeled, with two stomatic bands; apex acute. Cones conical, with slightly reflexed scales and short bracts, which sometimes protrude. A hybrid between *L. leptolepis* and *L. europaea.* The first cross grows with great vigour, and is not liable to attack by Larch Canker Fungus.

III.—TWIGS COVERED WITH A DENSE TOMENTUM.

12. *L. Lyallii,* Parlatore.—Lyall's Larch. North America. Twigs greyish in colour. Leaves ½–1½ in. long, stiff, tetragonal. Cones 1¼–2 in. long, with protruding reflexed bracts. A tree up to 80 feet in its native country. Of no economic value on account of its slow growth. Rare in cultivation.

8.—*PSEUDOLARIX.* GOLDEN LARCH.

A tree 100 feet high. *Branchlets* of two kinds: (1) long shoots, which continue growth; and (2) short secondary shoots or spurs, with annual zones of growth, each zone marked by a depression and a ring of subulate scales. *Leaves* arranged in two ways: (1) spirally, on the long shoots of the current season; and (2) in clusters of 15–30 at the apices of the short shoots; soft, annual, deciduous in autumn, linear, flattened; upper surface convex; lower surface keeled, with two stomatic bands; apex acuminate; resin-canals, three. *Buds* conical, surrounded by acuminate scales, with long subulate points. *Cones* erect on the branches, ovoid, with woody scales, ripening and falling to pieces in the first autumn. Seeds, white, with an ovate wing.

There is only one living species, *P. amabilis,* Nelson, a native of China, wild in two localities. It is hardy in the British Isles, but is rare in cultivation. Plate 9, fig. 8.

9.—*PINUS.* PINES.

Most species are large trees, yielding important commercial timber, but a few species are shrubs. *Branchlets* of two kinds: (1) short shoots or spurs of limited growth, bearing the adult leaves in clusters and deciduous with them; and (2) long shoots, the ordinary branchlets, which continue growth. *Leaves* of three kinds: (1) Primordial leaves, borne on seedling plants, solitary, spirally arranged, linear-lanceolate; (2) Scale leaves, containing in their axils the short shoots and adult leaves, triangular, usually quickly deciduous in part; and (3) Adult leaves, needle-like, persistent two to twenty years, in clusters of one to five (rarely six or seven) at the apex of the short shoot, serrulate or entire in margin; fibro-vascular bundle branched or simple; resin-canals, two to twelve, marginal or median. The sheath at the base of each cluster, formed by the scales of the minute buds, is either quickly and entirely deciduous or persistent. *Cones* woody, ripening in nearly all the species in the second year. Seeds, two on each scale, obovate, triangular or cylindrical; the wing embracing by its rim-like base the sides and upper surface of the seed.

About eighty species are known, and fifty-seven are in cultivation. Of these, only five—*P. sylvestris, P. Laricio, P. Austriaca, P. Pinaster,* and *P. radiata*—are suitable for economic planting in the British Isles. *Distribution*: northern hemisphere, from the Arctic Circle to Central America, the West Indies, Morocco, Algeria, Syria, Himalayas, Burma, Philippine Islands, Sumatra, and Borneo.

Pines do well on deep sands, loams, and gravels, and thrive on lowland peat if this is drained. As main crop trees, they should be planted close, and grown pure, and be thinned lightly only, as in this way the stems are pruned and the ground kept clean. They are liable to damage by weevils and other insects in the young stage, and suffer from diseases caused by Honey Fungus (*Armillaria mellea*), and Heart-rot Fungus (*Fomes annosus*). All the species mentioned above, except *P. sylvestris,* bear wind well, and are useful for planting in exposed situations, and for shelter-belts. See Nos. 27, 41, 47, 49, 53, 54, and 56. The timber of many of the pines is of great economic importance, and several are tapped for an oleo-resin, which by distillation yields rosin and turpentine.

The Pines are classified as follows:—

I.—HAPLOXYLON. SOFT PINES.

A. Strobus, White Pines:—*P. excelsa, P. Peuke, P. Ayacahuite, P. Lambertiana, P. monticola, P. Strobus, P. parviflora.*

B. Cembra, Stone Pines:—*P. Cembra, P. koraiensis, P. Armandi, P. pumila, P. flexilis, P. albicaulis.*

C. Gerardianae, Plane Bark Pines:—*P. Bungeana, P. Gerardiana.*

D. Cembroides, Nut Pines:—*P. monophylla, P. edulis, P. cembroides, P. Parryana.*

E. Balfourianae, Fox-tail Pines:—*P. Balfouriana, P. aristata.*

II.—DIPLOXYLON. HARD PINES.

F. Pseudostrobus:—*P. Montezumae, P. Hartwegii, P. pseudostrobus, P. Torreyana.*

G. Taeda:—*P. Coulteri, P. Sabiniana, P. ponderosa, P. Jeffreyi, P. tuberculata, P. radiata, P. patula, P. Teocote, P. rigida, P. serotina, P. palustris, P. Taeda, P. canariensis.*

H. Banksia:—*P. echinata, P. halepensis, P. muricata, P. pungens, P. virginiana, P. Banksiana.*

I. Pinaster:—*P. Pinaster, P. Pinea, P. sylvestris, P. densiflora, P. montana, P. contorta, P. resinosa, P. Thunbergii, P. Laricio, P. Austriaca, P. leucodermis.*

SPECIES IN CULTIVATION.

I.—LEAVES IN FIVES.

A.—Leaf-sheath entirely deciduous. Plate 9, fig. 6c.

(I).—Twigs glabrous.

1. *P. excelsa,* Wallich.—Blue Pine. Himalayas. Twigs glaucous green. Buds conic, shortly acuminate. Leaves 5–8 in. long, spreading, slender, some sharply bent as if broken. A tree up to 150 feet. Cultivated for ornament.

2. *P. Peuke,* Grisebach.—Macedonian Pine. Balkan Peninsula. Twigs shining green. Buds ovoid, shortly acuminate. Leaves about 4 in. long, densely tufted

towards the end of the branchlet, and not spreading or bent as in *P. excelsa*. A tree up to 100 feet. Cultivated for ornament.

3. *P. Armandi,* Franchet.—China. Twigs olive green, sometimes with minute scattered hairs. Buds with free or appressed scales. Leaves 4–6 in. long, spreading, and often bent as in *P. excelsa*. A tree up to 60 feet. Cultivated for ornament.

(II).—Twigs pubescent.

(a) Bud-scales free at their apices.

4. *P. Ayacahuite,* Ehrenberg. — Mexican White Pine. Mexico. Twigs covered with a short, rusty-brown pubescence. Buds ovoid, acuminate, resinous. Leaves 4–6 in. long, spreading, occasionally bent as in *P. excelsa*. A tree up to 100 feet. Rare in cultivation.

5. *P. flexilis,* James.—Western North America. Twigs glabrous, or covered with a minute, brown, soft pubescence. Buds ovoid, sharp-pointed, resinous. Leaves 2–3 in. long, stout, rigid, curved, sharp-pointed. A tree up to 50 feet. Rare in cultivation.

6. *P. albicaulis,* Engelmann. — Western North America. Scarcely distinguishable from *P. flexilis*; pubescence scattered, minute, stiff. A tree up to 80 feet. Rare in cultivation.

7. *P. Cembra,* Linnaeus. Cembra Pine. Alps, Siberia. Twigs covered with a dense orange-brown shaggy tomentum. Buds ovoid, acuminate, resinous. Leaves 2½–3½ in. long, with few serrations at the tip. Plate 9, fig. 6c. A tree up to 130 feet. Cultivated for ornament.

8. *P. koraiensis,* Siebold and Zuccarini. Korean Pine. Japan. Twigs and buds as in *P. Cembra*. Leaves with numerous sharp serrations at the tip, otherwise as in *P. Cembra*. A tree up to 150 feet.

9. *P. pumila,* Regel.—East Siberia and Japan. Twigs and buds as in *P. Cembra*. Leaves similar to that species, but entire in margin. A shrub, usually prostrate. Rare in cultivation.

(b) Bud-scales closely appressed.

10. *P. Lambertiana,* Douglas.—Sugar Pine. Oregon and California. Twigs with short brown, partly glandular, pubescence. Buds cylindrical, rounded at the apex, or sharp-pointed. Leaves about 4 ins. long, twisted, rigid, ending in a sharp cartilaginous point. A tree up to 200 feet. Cultivated for ornament.

11. *P. monticola,* Don.—Western White Pine. Western N. America. Twigs with short brown, partly glandular, pubescence. Buds ovoid, acuminate. Leaves 4 in. long, slightly twisted, blunt at the apex. A tree up to 100 feet. In cultivation as an ornamental tree.

12. *P. Strobus,* Linnaeus.—Weymouth Pine. Eastern N. America. Twigs with pubescent tufts below the insertions of the leaf-clusters, elsewhere usually glabrous. Buds ovoid, acuminate. Leaves 3 in. long, very slender, not twisted.

An important timber tree, up to 200 feet high, in North America. It is sometimes planted under forest conditions in the British Isles. It is liable to attack by aphis (*Chermes strobi*), and suffers severely from Pine Blister Rust (*Cronartium ribicola*).

13. *P. parviflora,* Siebold and Zuccarini.—Japanese White Pine. Japan. Twigs greyish, with a scattered minute pubescence. Leaves 1–2 in. long, slender, curved, margins finely serrulate; apex blunt, inner flat surface with three or four conspicuous white stomatic lines. A tree up to 100 feet. Cultivated for ornament.

B.—Leaf-sheath partly deciduous, the inner part persisting as a rosette of reflexed scales. Plate 9, fig. 6B.

14. *P. Balfouriana,* Balfour. — Foxtail Pine. California. Twigs stout, pubescent. Buds ovoid, acuminate. Leaves 1½ in. long, without stomata on the outer surface, rigid, curved. A tree up to 40 feet. Rare in cultivation.

15. *P. aristata,* Engelmann.—Foxtail Pine. South of N. America. Differs from the preceding species in the resinous exudation on the leaf. A tree up to 50 feet. Rare in cultivation.

C.—Leaf sheath persistent.

16. *P. Montezumae,* Lambert.—Mexico. Twigs stout, not glaucous, reddish brown. Buds ovoid, pointed, an inch long, reddish-brown, scarcely resinous. Leaves about 9 in. long; basal-sheaths 1¼–2 in. long. Scale-leaves persistent. A tree up to 70 feet. Rare in cultivation.

17. *P. Hartwegii,* Lindley. — Mexico. Twigs stout, not glaucous, reddish-brown. Buds ovoid, pointed, ½–¾ in. long, usually with resinous appressed scales. Leaves 5–6 in. long; basal-sheaths 1 in. long. Scale-leaves persistent. A tree up to 70 feet. Cultivated for ornament.

18. *P. pseudostrobus,* Lindley.—Mexico. Twigs slender, glaucous. Buds ovoid, pointed, scarcely resinous. Leaves about 9 in. long; basal-sheaths 1¼ in. long. Scale-leaves persistent. A tree up to 100 feet. Rare in cultivation.

19. *P. Torreyana,* Parry.—California. Twigs glaucous, dull grey in the second year. Buds cylindro-conic, ½ in. long; scales pale brown, with appressed points. Leaves 7–13 in. long, very stout; basal-sheath 1 in. long. Scale-leaves deciduous. A tree up to 60 feet. Rare in cultivation.

II.—LEAVES IN THREES.

A.—Leaf-sheath entirely deciduous.

20. *P. Bungeana,* Zuccarini. — China. Branchlets smooth, glabrous, green. Buds spindle-shaped, with scales free at their tips. Leaves 3 in. long, shining green, rigid, with the basal-sheaths deciduous in the first year. Bark smooth, scaling off in small plates like that of a plane tree. A tree up to 100 feet high. Rare in cultivation.

21. *P. Gerardiana,* Wallich.—Gerard's Pine. Western Himalayas. Branchlets smooth, glabrous, green. Buds conic, acuminate, resinous. Leaves 3–4 in. long, duller in colour and less rigid than in *P. Bungeana,* with the basal-sheath deciduous in the second year. Bark smooth, scaling off in small plates like that of a plane tree. A tree up to 80 feet high. Rare in cultivation.

B.—Leaf-sheath persistent.

(I).—Buds resinous; points of bud-scales appressed.

(a) Leaves more than 6 in. long.

22. *P. Coulteri,* Don.—Coulter's Pine. California. Branchlets stout, glaucous, remaining green in the second year. Buds ovoid, stout, acuminate or cuspidate, 1–1½ in. long. Leaves 10–14 in. long, dark green, spreading from the upper part of the branchlets of the first and second years. A tree up to 80 feet high. Cultivated for ornament.

23. *P. Sabiniana,* Douglas.—Digger Pine. California. Branchlets slender, glaucous, remaining green in the second year. Buds narrowly cylindrical, an inch long. Leaves 7–12 in. long, greyish green, spreading or drooping from the upper part of the branchlets of the first and second years. A tree up to 50 feet. Cultivated for ornament.

24. *P. ponderosa,* Lawson.—Yellow Pine. Western North America. Branchlets stout, reddish, not glaucous, becoming dark brown in the second and third years. Buds cylindro-conic, an inch long. Leaves 6–10 in. long, dark green, densely crowded on the greater part of the branchlets, directed outwards and forwards. An important timber tree in its native country. In cultivation as an ornamental tree.

25. *P. Jeffreyi,* Vasey.—Jeffrey's Pine. California. Branchlets stout, glaucous, becoming dark-coloured in the second and third years. Buds stout, cylindro-conic, an inch long, with scales less resinous and their points more free than in *P. ponderosa.* Leaves 6–10 in. long, directed outwards and forwards. A tree up to 120 feet. Cultivated for ornament.

(b) Leaves less than 6 in. long.

26. *P. tuberculata,* Gordon. — Knob-cone Pine. Oregon and California. Branchlets reddish-brown, not glaucous. Buds cylindrical, pointed, an inch long. Leaves 4–5 in. long, rigid, dark green; basal-sheath ½ in. long. A tree up to 50 feet. Cultivated for ornament.

27. *P. radiata,* Don (*P. insignis,* Douglas).—Monterey Pine. California. Branchlets reddish-brown, not glaucous. Buds cylindrical, pointed, ½–¾ in. long. Leaves 4–5 in. long, slender, flexible and soft in texture, light green, densely crowded on the branchlets; basal-sheath ½ in. long. A tree up to 100 feet high. Invaluable for commercial planting and for shelter-belts in the milder parts of England, Wales, Ireland, and south-west Scotland, growing at a remarkably fast rate, and producing a large volume of coarse, soft timber. It succeeds in

mild localities near the sea-coast in poor, dry, and stony soils, provided they do not contain more than a small percentage of lime.

(II).—Points of bud-scales free, and slightly spreading, not reflexed.

28. *P. patula,* Schlechtendal and Chamisso.—Mexico. Branchlets glaucous. Buds cylindro-conic, ½–¾ in. long. Leaves, 6–9 in. long, filiform, soft, and very slender, drooping; basal-sheath, 1 in. long. Bark on the upper part of tree reddish, and peeling off in thin papery flakes, like that of *P. sylvestris.* A tree up to 80 feet high. In cultivation in the milder parts of the British Isles as an ornamental tree.

29. *P. Teocote,* Schlechtendal and Chamisso.—Mexico. Branchlets glaucous, the epidermis of the decurrent pulvini peeling off in the second and third years. Buds cylindro-conic, resinous, ¾ in. long. Leaves, 4–8 in. long, rigid, spreading; basal-sheath an inch long. A tree up to 80 feet. In cultivation in the warmer and milder parts of the British Isles as an ornamental tree.

30. *P. rigida,* Miller. — Eastern Canada and North-Eastern United States. Branchlets not glaucous. Buds cylindro-conic, ½–¾ in. long. Leaves, 3½–4 in. long, rigid; basal-sheath, ⅜–½ in. long. A tree up to 80 feet. Cultivated for ornament.

31. *P. serotina,* Michaux.—Pond Pine. South-east and South United States. Distinguished from *P. rigida* by the more resinous buds and longer leaves, 6–10 in. long; but in cultivated trees in the British Isles the leaves are as short as in that species. A tree up to 80 feet. In cultivation in the milder parts of the British Isles as an ornamental tree.

(III).—Buds non-resinous; bud-scales with free, fimbriated and recurved points. The apex of the second year's branchlet is marked with a sheath of persistent, recurved, bud-scales.

32. *P. palustris,* Miller.—Long-leaf Pine. Pitch Pine. South-east and South United States. Branchlets stout, orange-brown. Buds 1½–2 in. long, with silvery white scales. Leaves, 8–18 in. long, densely crowded on the branchlets; basal-sheath ⅗–1 in. long. Scale-leaves persistent. A tree up to 120 feet high. An important timber tree in its native country. It is too tender for cultivation in the British Isles.

33. *P. Taeda,* Linnaeus.—Loblolly Pine. South-east United States. Branchlets glaucous. Buds ½ in. long, with brown scales. Leaves, 6–9 in. long, spreading; basal-sheath nearly 1 in. long. Scale-leaves persistent. A tree up to 100 feet high. An important timber tree in its native country. It is too tender for cultivation in the British Isles, but may be grown for ornament in the milder parts of England, Wales, and Ireland.

34. *P. canariensis,* Smith.—Canary Pine. Canary Islands. Branchlets yellow, not glaucous. Buds ¾ in. long, with reddish-brown scales. Leaves,

7–12 in. long, densely crowded on the branchlets, slender, flexible. A tree up to 80 feet. Cultivated for ornament in mild localities.

III.—LEAVES SOLITARY, OR IN TWOS, THREES, OR FOURS ON THE SAME BRANCH.

A.—Leaf-sheaths partly deciduous, their inner part persisting as a rosette of reflexed scales around the base of the leaf-bundle. Leaves entire in margin. Plate 9, fig. 6B.

35. *P. monophylla,* Torrey.—One-leaf Nut Pine. Western United States. Leaves solitary, rigid, terete, sharp-pointed, 1½ in. long, remotely placed on the branchlets. A tree up to 30 feet. Cultivated for ornament.

36. *P. edulis,* Engelmann.—Western United States. Leaves in twos, rarely in threes, rigid, sharp-pointed, ¾–1½ in. long, remotely placed on the branchlets. A tree up to 20 feet high. Cultivated for ornament.

37. *P. cembroides, Zuccarini.*—Western United States. Leaves in threes, rarely in twos, softer and more slender than in the other species of the section, and densely crowded on the branchlets. Plate 9, fig. 6B. A tree up to 20 feet high. Cultivated for ornament.

38. *P. Parryana,* Engelmann.—California. Leaves in fours, rarely in fives, 1½ in. long, rigid, sharp-pointed, remotely placed on the branchlets. A tree up to 20 feet high. Cultivated for ornament.

B.—Leaf-sheaths persistent.

39. *P. echinata,* Miller (*P. mitis,* Michaux).—Short-leaf Pine. South-eastern United States. Leaves in twos and in threes. Branchlets slender, brittle, glaucous. Buds ¼ in. long, brownish, shining, with resinous appressed scales. Leaves, 3 in. long; resin-canals median; basal-sheath ⅜ in. long. Plate 15, fig. 71A. A tree up to 120 feet high. Rare in cultivation.

IV.—LEAVES IN PAIRS. LEAF-SHEATH PERSISTENT. Plate 9, fig. 6A.

A.—Buds non-resinous, bud-scales with free and recurved points.

40. *P. halepensis,* Miller.—Aleppo Pine. Mediterranean region. Caucasus. Branchlets glaucous. Leaves 2½–4 in. long; resin-canals marginal; basal-sheath ⅛ in. long. In var. *Brutia* the leaves are 4–6 in. long. A tree up to 80 feet high. Cultivated for ornament.

41. *P. Pinaster,* Solander.—Maritime Pine. Mediterranean region. Branchlets stout. Buds stout, spindle-shaped, pointed, ¾–1 in. long. Leaves, 5–6 in. long, stout, rigid; resin-canals median; basal-sheath 1 in. long. A tree up to 120 feet. Planted on the shifting sand-dunes of the Landes, in south-western France, yielding by tapping large quantities of resin, which is distilled to extract rosin and turpentine. The timber is used for telegraph poles and pit-props. It is useful for the afforestation of sand-dunes, and well-drained cut-away lowland bogs in the milder parts of England and Ireland, and bears the

wind well when planted near the sea-coast. It is not suitable for northern localities inland or at high elevations.

42. *P. Pinea,* Linnaeus.—Stone Pine. Mediterranean region. Branchlets slender. Buds ovoid, pointed, $\frac{3}{8}$ in. long. Leaves 4–5 in. long; resin-canals marginal; basal-sheath $\frac{4}{10}$ in. long. A tree up to 100 feet. Cultivated for ornament.

B.—Buds resinous.

(I) Bud-scales appressed.

(a) Buds cylindric or spindle-shaped.

43. *P. muricata,* Don.—Bishops' Pine. California. Branchlets stout, reddish-brown. Buds cylindrical, $\frac{3}{4}$–1 in. long; scales encrusted with white resin. Leaves 4–6 in. long, stout, rigid; resin-canals median; basal-sheath $\frac{1}{2}$ in. long. A tree up to 50 feet high. Hardier than *P. radiata,* succeeding under similar conditions, but less vigorous in growth and suffering greatly from attacks of the Pine-shoot Moth (*Retinia resinella*). Usually cultivated for ornament.

44. *P. Pungens,* Michaux.—Alleghany Mountains. Branchlets shining brown. Buds cylindrical, $\frac{3}{4}$ in. long. Leaves 2–2$\frac{1}{2}$ in. long, stout, rigid, very sharp-pointed; resin-canals median; basal-sheath $\frac{1}{4}$ in. long. A tree up to 60 feet high. Cultivated for ornament.

45. *P. virginiana,* Miller.—Jersey Pine, Scrub Pine. Eastern United States. Branchlets slender, glaucous, violet. Buds cylindrical, $\frac{3}{8}$ in. long. Leaves 1$\frac{1}{2}$–3 in. long; resin-canals median; basal sheath $\frac{3}{10}$ in. long. A tree up to 40 feet high. Cultivated for ornament.

46. *P. sinensis,* Lambert.—Chinese Pine. China. Branchlets light brown. Buds ovoid-oblong, 1$\frac{1}{4}$ in., pointed, shining brown, with closely pressed scales. Leaves 4–6 in. long, margins finely toothed, apex sharp, horny; spreading, persistent, four years; resin-canals marginal; basal-sheath about $\frac{1}{4}$ in. long. Plate 15, figs. 71c and 73. A tree up to 100 feet. Cultivated for ornament.

47. *P. montana,* Miller.—Mountain Pine. Mountains of Central and Southern Europe. Branchlets brown. Buds $\frac{1}{4}$–$\frac{1}{2}$ in. long, very resinous. Leaves 1$\frac{1}{2}$–2$\frac{1}{2}$ in. long, persistent 5–10 years; resin-canals marginal; basal sheath $\frac{1}{2}$–$\frac{6}{10}$ in. long. Plate 15, fig. 74. A tree or a prostrate shrub. The taller form, var. *uncinata,* Willkomm, grows to be a tree up to 80 feet high. Useful for planting on peaty soil in exposed situations and at high elevations, as a help to establish more valuable species. May be planted as a shelter-belt on wet peaty soils.

48. *P. contorta,* Loudon.—Shore Pine. Coast of western North America. Branchlets brown. Buds $\frac{1}{2}$ in. long, encrusted with resin. Leaves persistent, 3–8 years, twisted, 1$\frac{1}{2}$–3 in. long; resin-canals median; basal-sheath $\frac{1}{4}$ in. long. Plate 15, fig. 75. A tree up to 30 feet high. In cultivation.

49. *P. Murrayana,* Balfour.—Lodgepole Pine. Mountains of western North America. Branchlets brown. Buds $\frac{1}{6}$ in. long, resinous. Leaves persistent, 3–8 years, slightly twisted, 1$\frac{1}{2}$–3 in. long; resin-canals median; basal-sheath

¼ in. long. A tree up to 100 feet high. Useful for commercial planting in the British Isles, where it succeeds on dry, gravelly soils or on drained peat.

(*b*) *Buds ovoid.*

50. *P. Banksiana,* Lambert.—Jack Pine. Eastern North America. Branchlets slender, greenish. Buds ½ in. long. Leaves olive green, 1 in. long; resin-canals median; basal-sheath ⅛–¼ in. long. A tree usually small, but in rare cases 90 feet in height. Cultivated for ornament.

51. *P. resinosa,* Aiton.—Eastern North America. Branchlets orange-brown. Buds pale brown, ½–¾ in. long. Leaves persisting 4 years, 5–6 in. long; resin-canals marginal; basal-sheath ⅞ in. long. A tree up to 90 feet high. An important timber tree in its native country. Cultivated for ornament.

52. *P. Thunbergii,* Parlatore.—Japan. Branchlets brown. Buds ½–¾ in. long, greyish white. Leaves 3–4 in. long, rigid, sharp-pointed; resin-canals median; basal-sheath ½ in. long, ending above in two long filaments. A tree up to 130 feet high. An important timber tree in its native country. Usually cultivated for ornament in the British Isles, but suitable for plantations on sandy soil near the sea-coast.

53. *P. Laricio,* Poiret.—Corsican Pine. Corsica, Spain, South of France, Calabria. Branchlets brown. Buds ½–1 in. long, light brown, tinged with white. Leaves persisting 3 years, 4–6 in. long; flexible, bending easily when held at half their length and lightly tapped at the apex; resin-canals median; basal-sheath ½ in. long. Plate 15, figs. 71B and 76. A tree up to 150 feet high. A much more vigorous species than Scots Pine in most parts of the British Isles, producing a considerably larger volume of timber. It grows freely in dry situations and in soil containing lime, and even succeeds on clay. It bears constant wind well, and is valuable for planting in shelter-belts near the sea-coast and in hilly districts. Young trees have a poor root system, and require to be planted in their permanent sites as seedlings, or moved every year in the nursery until ready for planting out.

54. *P. austriaca,* Hoess.—Austrian Pine. Austria, Balkan States, and Crimea. Branchlets brown. Buds ½–1 in. long, greyish white. Leaves dark green, persisting 5–6 years, 4–6 in. long, rigid, not bending easily when held at half their length and lightly tapped at apex; resin-canals median; basal-sheath ½ in. long. A tree up to 60 feet high. Not suitable for commercial planting in the British Isles, the timber being coarse, rough, and knotty. It forms a tree with dense foliage, and is useful for shelter-belts near the sea-coast and on exposed hillsides of chalk or limestone.

55. *P. leucodermis,* Antoine.—Bosnia, Montenegro. Branchlets glaucous. Buds ½–1 in. long, dark brown. Leaves dark green, 2–3 in. long, rigid, sharp-pointed; basal-sheath ½ in. long. A tree up to 90 feet high. Cultivated for ornament.

(II) Bud-scales free at the apex. Bark of upper part of stem reddish, and peeling off in thin papery scales.

56. *P. sylvestris*, Linnaeus.—Scots Pine. Europe, Asia Minor, Caucasus, Siberia. Branchlets shining, greenish. Buds oblong-ovate, ¼–½ in. long, pointed. Leaves 2–3 in. long, glaucous blue, broad and flattened, usually twisted; resin-canals marginal; basal-sheath ⅓ in. long. A tree up to 100 feet high. Valuable for commercial planting in the British Isles, where it gives a good return when planted pure on deep dry soil, in situations not exposed to the prevailing wind.

57. *P. densiflora*, Siebold and Zuccarini.—Japan. Branchlets glaucous. Buds ½ in. long. Leaves 3–4 in. long, dull green; resin-canals marginal; basal-sheath ⅜ in. long, often ending in two long narrow filaments. A tree up to 120 feet high. An important forest tree in its native country, occupying there a similar position to *P. sylvestris* in North Europe. Rare in cultivation.

ARAUCARINEAE.

10.—*AGATHIS.* KAURI PINES.

Usually tall trees. *Leaves* spirally arranged on the main axis, opposite or sub-opposite on lateral branchlets; large, ovate, ovate-lanceolate, or lanceolate, with many parallel veins, between which lie the resin-canals; both surfaces finely striated longitudinally, with no apparent stomata when examined with a lens; apex blunt, sessile, or with a short, flat stalk. *Cones* globular or oval, 3–4 in. in diameter, compact, with woody scales; ripening in 2 or 3 years, and falling in pieces when ripe. Seeds, one on each scale, not adnate to it, with usually only one wing.

About eighteen species have been described, some of which are perhaps Caledonia, Fiji, Philippine Islands, Solomon Islands, New Hebrides, and Malay Peninsula and Archipelago.

The Kauri Pines are important forest trees in their native countries, yielding valuable timber and resin. The wood is yellowish in colour, and very resinous. It is of good quality, is easily worked, and is used for building purposes. In the British Isles the cultivation of Agathis is restricted to greenhouses and outdoors in mild localities.

SPECIES IN CULTIVATION.

1. *A. australis*, Salisbury.—Kauri Pine. New Zealand. Leaves lanceolate, 1–3 in. long and ¼–½ in. wide; margins not recurved. Plate 12, fig. 35. Up to 120 feet high.

2. *A. robusta*, Masters.—Queensland Kauri Pine. Australia. Leaves ovate-lanceolate, thick, 4–6 in. long, and 1–2 in. wide; margins thickened and recurved. Up to 150 feet high.

3. *A. vitiensis,* Bentham and Hooker. — Fiji. Leaves ovate or ovate-lanceolate, 2–5 in. long, ⅓–1½ in. wide, sometimes glaucous beneath; margins not recurved. Up to 50 feet high.

The following species have not been introduced:—

A. loranthifolia, Salisbury.—Malaya and Polynesia.
A. macrophylla, Masters.—Solomon Islands and Polynesia.
A. Moorei, Masters.—New Caledonia.
A. ovata, Warburg.—New Caledonia.
A. lanceolata, Pancher.—New Caledonia.
A. Palmerstoni, Von Mueller.—Queensland.
A. philippinensis, Warburg.—Philippine Islands.
A. Beccarii, Warburg.—Borneo.

11.—*ARAUCARIA.*

Usually tall trees. *Leaves* spirally arranged. Different in the two sections of the genus:—(*a*) large, ovate-lanceolate or lanceolate; and (*b*) small and awl-shaped. *Cones* globular, 2–9 in. in diameter, with imbricated wedge-shaped woody scales, thickened at the apex; ripening in two or three years, and falling to pieces when ripe. Seeds, one on each scale, and adnate to it, and usually with a wing on each edge.

About fourteen species have been described. *Distribution*: South America, Australia, New Guinea, New Hebrides, New Caledonia, and Norfolk Island.

Most of the Araucarias are important forest trees in their native countries, growing to a large size, and yielding valuable timber. The wood is soft, resinous, straight-grained, easily worked, and is used for furniture manufacture and for all kinds of indoor work, and for paper-pulp. *Araucaria imbricata* is the only species which is hardy in the British Isles. The cultivation of the other species is restricted to greenhouses, and out of doors in the milder parts of the south of England and Ireland.

SPECIES IN CULTIVATION.

I.—SECTION COLYMBEA.

Leaves large, flattened, ovate-lanceolate or lanceolate, with many parallel veins between which lie the resin-canals; sessile, coriaceous, rigid; upper surface bright shining green, slightly concave; lower surface dull green, convex; both surfaces finely striated, and having stomatic lines plainly visible with a lens; apex acuminate, with a sharp cartilaginous point.

1. *A. imbricata,* Pavon.—Chile Pine. Chile. Leaves densely imbricate on all the branches, ovate-lanceolate, 1–1½ in. long, ¾–1 wide, dark green, very rigid. Up to 150 feet high. An important forest tree.

2. *A. Bidwillii,* W. Hooker. — Bunya-Bunya. Queensland. Leaves on fruiting branches imbricate, on sterile branches arranged in two sets, lanceolate,

¾–1½ in. long, ¼–⅜ in. wide, light green, thinner and less rigid than those of *A. imbricata.* Plate 12, fig. 34. Up to 150 feet high. An important forest tree.

3. *A. brasiliana,* A. Richard.—Candelabra Tree. Brazil. Leaves on fruiting branches densely imbricate, on sterile branches arranged in two sets, lanceolate; on young trees 1½–2½ in. long, ⅜–½ in. wide; on older trees ¾–1 in. long, ⅛–¼ in. wide; lower surface glaucous. Up to 100 feet high. An important forest tree.

II.—SECTION EUTASSA.

Leaves awl-shaped, curved, broad at the base, and narrowing towards the apex; resin-canals scattered through the substance of the leaf. Leaves on juvenile plants rhombic in cross-section, slightly flattened laterally; stomatic lines on all four surfaces; on adult trees, flattened from above downwards; ventral surface concave, with stomatic lines; dorsal surface convex, with or without stomatic lines.

4. *A. Cunninghamii,* Aiton.—Moreton Bay Pine. Australia. Leaves light green, somewhat glaucous; on young plants ⅓–¾ in. long, with sharp cartilaginous points; on adult trees shorter and stouter, with a short-pointed, incurved apex. Plate 10, fig. 18. Up to 200 feet high. An important forest tree.

5. *A. excelsa,* R. Brown.—Norfolk Island Pine. Norfolk Island. Leaves bright green, not glaucous; on young plants up to ½ in. long; on adult trees ¼ in. long, and ¼ in. wide at the base, with an incurved horny point. Up to 200 feet high. Of small economic importance.

6. *A. Cookii,* R. Brown (*A. columnaus,* Hooker).—New Caledonia. Leaves dark green, not glaucous; on young plants ½ in. long; on adult trees ¼ in. long, and ⅜ in. wide at the base, with a blunt incurved point; stomatic lines on the dorsal surface near the base. Plate 14, fig. 59. Up to 200 feet high. Of small economic importance.

7. *A. Balansae,* Brongniart and Gris (*A. elegans,* Hort.)—New Caledonia. Leaves on young trees up to ½ in. long and ⅛ in. wide; on adult trees ⅛ in. long, and ⅛ in. wide; apex acuminate; without stomatic lines on the dorsal surface. Up to 60 feet high. Of no economic importance.

8. *A. Rulei,* Von Mueller.—New Caledonia. Leaves on young plants up to ¾ in. long, on adult trees ½ in. long, and ⅜ in. wide; apex short-pointed, abruptly incurved; stomatic lines on the dorsal surface. Up to 50 feet high. Of no economic importance.

The following species have not been introduced into cultivation:—

9. *A. Beccarii,* Warburg.—New Guinea.
10. *A. Muelleri,* Brongniart and Gris.—New Caledonia.
11. *A. Hunsteinii,* K. Schum.—New Guinea.
12. *A. Schumanniana,* Warburg.—New Guinea.
13. *A. Kleinkii,* Laut.—New Guinea.
14. *A. Montana,* Brongniart and Gris.—New Caledonia.

12.—*CUNNINGHAMIA.*

Trees up to 180 feet high. *Leaves* spirally arranged, usually twisted, to form two ranks; narrowed at the base and decurrent on the twig; rigid, more or less curved, narrowly lanceolate, acuminate; upper surface dark green, concave, with slightly raised margins; lower surface convex, with a green midrib and two stomatic bands; edge sharply and finely serrate; fibro-vascular bundle unbranched, with a single resin-canal beneath it. *Cones* ovoid-globose, about $1\frac{1}{2}$ in. long, with thin, woody, loosely imbricated scales. Seeds, three on each scale, about $\frac{1}{4}$ in. long, brown, oblong, compressed, surrounded by a membraneous narrow wing.

Two closely related species are known, occurring in China and Formosa.

The Chinese species is a valuable tree in its native country. The wood is light, soft, pale yellow, or almost white, easily worked, durable, and is used for house-building and other purposes. It is hardy in the milder parts of England and Ireland, and is grown for ornament. The Formosan species has been introduced, but is still rare in cultivation.

1. *C. sinensis,* R. Brown. — China. Leaves 1–$2\frac{3}{4}$ in. long, $\frac{1}{8}$–$\frac{1}{6}$ in. wide; stomatic lines on upper surface inconspicuous or absent. Plate 12, fig. 33.

2. *C. Konishii,* Hayata. — Formosa. Leaves $\frac{3}{4}$–$1\frac{1}{4}$ in. long, $\frac{1}{10}$–$\frac{1}{8}$ in. wide; stomatic lines on upper surface conspicuous.

13.—*TAIWANIA.*

A tree up to 200 feet high. *Leaves* spirally arranged, curved, $\frac{1}{5}$ in. long, decurrent, and broad at the base, gradually narrowing towards the apex; trigonous in cross-section, with longitudinal stomatic hollows on all three surfaces; apex incurved, mucronate. Leaves on young trees $\frac{1}{2}$ in. long, sharp-pointed, straight, or slightly curved. *Cones* shortly cylindrical, $\frac{1}{2}$ in. long, with numerous overlapping, mucronate scales. Seeds, two on each scale, oblong, broadly winged.

Only one species, *T. cryptomerioides,* Hayata, is known, occurring on the western slope of Mount Morrison, Formosa, at 6,000–8,000 feet elevation. It has been introduced, but is rare in cultivation. Plate 10, figs. 15 and 16.

TAXODINEAE.

14.—*ATHROTAXIS.*

Usually large trees. *Leaves* spirally arranged, imbricate, spreading or closely appressed. *Cones* spherical, $\frac{1}{4}$–$\frac{3}{4}$ in. in diameter; scales woody, ending in a spine-like process. Seeds, three to six on each scale, pendulous from the thickened part of the scale below the apex; thin, oblong, with two narrow wings; ripening in one year.

Three species are known, natives of Tasmania, all introduced, and forming handsome, hardy, vigorous trees.

Athrotaxis is of small economic value. The wood is pinkish, open, and straight-grained, light in weight, easy to work, and is used in Tasmania for cabinet-making, coach-building, and the internal finish of houses.

I.—Leaves spreading, entire in margin, rigid, trigonous, with two continuous white stomatic bands on the concave ventral surface, and two lateral stomatic depressions near the base on the convex dorsal surface.

1. *A. selaginoides,* Don.—Leaves very spreading, $\frac{1}{4}$ in. long, with a rigid, spine-like, acuminate apex, and an opaque margin. Up to 100 feet high. Plate 10, fig. 19.

2. *A. laxifolia,* W. J. Hooker.—Leaves slightly spreading, $\frac{1}{4}$ in. long, obtuse or acute at the apex, and with a translucent margin. Up to 40 feet high. Plate 10, fig. 20.

II.—Leaves closely appressed, scale-like; margin translucent and denticulate; ventral surface concealed; dorsal surface with indistinct stomatic lines.

3. *A. cupressoides,* Don.—Leaves rhombic-ovate, obtuse at the apex, $\frac{1}{8}$ in. long. Up to 40 feet high. Plate 10, fig. 12.

15.—*SEQUOIA.*

A large tree, up to 360 feet high. *Leaves* spirally arranged:—(*a*) on normal branchlets spreading in one plane, $\frac{1}{4}$–$\frac{3}{4}$ in. long, linear or lanceolate, ending in a short cartilaginous point; narrowed at the base, decurrent on the twigs; upper surface dark green, with a median furrow; lower surface with a green midrib and two conspicuous stomatic bands; central resin-canal; and (*b*) on leading branchlets, radially arranged in several ranks, about $\frac{1}{4}$ in. long, ovate or ovate-oblong, with incurved cartilaginous points. *Buds* small, solitary, surrounded by loose scales, which turn brown and persist as a ring at the base of the branchlets during several years. *Cones* pendulous, ellipsoidal, about 1 in. long; scales persistent, woody, wedge-shaped at the base, widening towards the apex, with a central depression. Seeds, 5–7 on each scale, pendulous, oblong-ovate, compressed, with two lateral wings. Cones ripening in the first autumn, and remaining on the tree after the fall of the seeds.

One living species, *S. sempervirens,* Endlicher, is known, occurring in the coast range in California. The allied *Wellingtonia gigantea* is usually united with *Sequoia,* which is considered by most writers to embrace two living species. Plate 10, fig. 23.

Sequoia sempervirens grows to an enormous size in California, yielding timber of large dimensions. The wood is soft, fine-grained, deep reddish-brown, with numerous resin-cells, durable, easy to work, and is used for house-building, telegraph poles, railway sleepers, furniture manufacture, and for many other

purposes. It is common in cultivation as an ornamental tree, and grows well in sheltered situations in the milder parts of England and Ireland.

16.—*WELLINGTONIA.*

A large tree, attaining 320 feet. *Leaves* up to ¼ in. long, curved, decurrent, and broad at the base, gradually narrowing towards the apex; triangular in cross-section, with a central resin-canal; ventral surface with a green midrib and two white stomatic bands; dorsal surface with scattered, indistinct stomatic lines; apex sharp-pointed. *Cones* pendulous, ovoid, 2–3 in. long. Scales persistent, woody, wedge-shaped at the base, widening towards the apex, with a central depression. Seeds, 5–7 on each scale, flat, thin, oblong, margined by a narrow wing. Cones ripening in the second autumn, and remaining on the tree after the fall of the seeds.

Only one species is known, *W. gigantea,* Lindley (or more usual in text-books *Sequoia gigantea,* Torrey). It is a native of the mountains of California, where it is called "Big Tree." Plate 10, fig. 17.

Wellingtonia grows to an enormous size in California, yielding valuable timber of large dimensions. The wood is soft, deep reddish-brown in colour, with numerous resin-cells, durable, somewhat brittle. The timber is not plentiful, owing to the limited number of trees available, and is used locally for general purposes. It is common in cultivation as an ornamental tree, and grows freely in situations too exposed for *Sequoia sempervirens.*

17.—*CRYPTOMERIA.*

A tree up to 120 feet high. *Leaves* spirally arranged, curved, tetragonal, decurrent, and broad at the base, gradually narrowing towards the apex; stomatic lines on all four surfaces; large central resin-canal. *Cones* solitary, globular, ½–¾ in. in diameter, with 20–30 loosely imbricated scales. Seeds dark brown, triangular, up to ¼ in. long. Cones ripening in the first autumn, and persisting on the tree after shedding the seeds.

There is only one species, *C. japonica,* D. Don, a native of China and Japan. Plate 10, fig. 14.

Cryptomeria is an important forest tree, and is one of the most commonly grown conifers in Japan. The wood is coarse-grained, with a red heartwood, and is strong, durable, and easy to work. The timber is used in house-building, furniture manufacture, and for all kinds of indoor work. It is hardy in the British Isles, and is cultivated as an ornamental tree, growing well in sheltered situations.

18.—*GLYPTOSTROBUS.* CHINESE SWAMP CYPRESS.

A tree up to 80 feet high, with woody "knees," which grow up from the roots and project above the surface of the ground around the tree. *Branchlets* of two kinds, annual and perennial, the former falling with the leaves in the autumn of the first year, the latter continuing growth, remaining green for

several years, and bearing white stomatic dots. *Leaves* of three kinds:—(*a*) linear, flat, very thin, acute at the apex, and contracted at their attachments to the branchlets, on which they are decurrent; upper surface green; lower surface with lines of stomatic dots on each side of the prominent midrib; (*b*) acicular, curved or falcate, quadrangular in cross-section; and (*c*) scale-like, convex on the back, which shows numerous stomatic dots and a conspicuous median furrow. *Cones* erect and terminal on the branchlets, pyriform, ½–1 in. long; scales, 20, oblong, imbricated by their overlapping edges, attached by their stipes to a disc on the top of the branchlet; no resin pockets. The cones ripen in the second year, and remain on the tree after the scales gape apart to allow the seeds to escape. Seeds ovoid, small, with a long terminal wing.

Only one species, *G. pensilis*, Koch, survives in the living state, restricted to two small areas in China. Plate 11, fig. 31.

Glyptostrobus is of no economic value. It has been introduced and is hardy in the milder parts of England and Ireland, but is rare in cultivation.

19.—*TAXODIUM*. AMERICAN SWAMP CYPRESSES.

Trees, often with woody "knees," which grow up from the roots, and project above the surface of the ground around the tree. *Branchlets* of two kinds—annual and perennial; the former falling with the leaves in the autumn of the first year, the latter continuing growth, and becoming brown and corky in the second year. *Leaves* of two kinds:—(*a*) acerose on the perennial branchlets, ovate or lanceolate, broad at the truncate, sessile base; apex acuminate, tipped with a long, often bent and hook-like, cartilaginous mucro; compressed; upper surface flat, with a median furrow; lower surface convex; each surface with two indistinct stomatic bands; and (*b*) linear, nearly of the same width throughout, but contracted at the base into a short petiole-like part, and acute at the apex, which is tipped with a minute cartilaginous mucro; upper surface green or glaucous, with or without a stomatic band on each side of a median furrow; lower surface flat, and with two broad bands of stomata plainly visible. *Cones* globose or ellipsoidal, 1–1¼ in. in diameter, attached laterally by a minute stalk to the branchlet; scales, twenty, rhomboidal, joined together by their edges without overlapping; stipes of the scales attached to a slender conical axis; resin-pockets large and conspicuous. The cone ripens in the first autumn, and falls to pieces, the scales separating from each other, and falling with the seeds. Seeds large, trigonous, unwinged.

Three species have been described, occurring in the South-Eastern United States and Mexico.

Taxodium is of economic importance in its native country, where the timber is used for house-building, cooperage, and railway sleepers. The wood is pale to dark brown in colour, light in weight, easily worked, durable. The three species are hardy in the British Isles, and are in cultivation as ornamental trees.

1. *T. distichum,* Richard. — South-Eastern United States. Acerose and linear leaves occur. Cone dull, without bloom, and with indistinct grooves above the mucros of the scales. Knees frequently developed. Up to 150 feet high. Plate 11, fig. 32.

2. *T. adscendens,* Brongniart.—South-Eastern United States. Differs from *T. distichum* in having only acerose leaves, and is considerably less vigorous in growth. Probably a sport of *T. distichum.* Up to 100 feet high.

3. *T. mucronatum,* Tenore.—Mexico. Differs from *T. distichum* in the more persistent annual branchlets, and in the glaucous cones, with distinct grooves and ridges on the cone-scales. It is said not to develop knees. Up to 100 feet high. Rare in cultivation.

20.—*SCIADOPITYS.* UMBRELLA PINE.

A tree up to 120 feet high. The branches bear *cladodes* (i.e., branchlets stimulating leaves in appearance, and functioning like true leaves). The cladodes are arranged in false whorls at the nodes, and are 2–5 in. long, rigid, furrowed above, and grooved beneath. The true *leaves* are reduced in minute scales, borne spirally on the internodes. *Cones* oblong-ovoid, 2½–4 in. long, and 1½–2 in. in diameter, with short stalks and persistent woody scales. Seeds, 5–9 on each fertile scale, oblong or elliptical, up to ½ in. long, surrounded by a narrow wing.

There is only one living species, *S. verticillata,* Siebold and Zuccarini—a native of Japan. It has been introduced, but is rare in cultivation. Plate 13, fig. 39.

Sciadopitys is an important tree in Japan, where the timber is used for boat-building, cooperage, and similar purposes. The wood is brownish yellow in colour, straight-grained, strong, durable, and easily worked.

CUPRESSINEAE.

21.—*CUPRESSUS.* CYPRESSES.

Trees, or rarely shrubs, usually with the terminal shoot bending over at the tip. *Branches* terminating in so-called "branchlet-systems," which are 2-, 3-pinnately divided, their primary and other axes being densely covered by the scale-like leaves, arranged in opposite decussate pairs. *Cones* globose, with 4–14 woody peltate scales, abruptly dilated at the apex, each with a central process. Seed, erect on the base of the scale, angled, compressed or rounded, with two thin lateral wings.

There are about eighteen species, of which only two, *C. Lawsoniana* and *C. macrocarpa,* are suitable for commercial planting in the British Isles. Most of the other species are in cultivation as ornamental trees. *Distribution*: North America, Mexico, India, Himalayas, China, Japan.

Cypresses thrive on any soil provided it is well drained, growing well on limestone, sand, or peat. They may be planted in mixture with beech or other

species, but succeed best when grown pure. They are intense shade-bearers, cleaning their stems with great difficulty, and even when spaced at four feet apart may require artificial pruning. See Nos. 5 and 29 in special key. The timber of most species is very valuable. It is remarkably durable, lasting indefinitely in water, and is used for house-building, telegraph poles, furniture manufacture, and other purposes. The wood is yellow to light brown in colour, without resin-ducts, fine-grained, and is easily worked.

The genus is divided into two sections:—

I.—EU-CUPRESSUS.

Leaves with a microscopic translucent border, either uniform in four ranks and similar in shape, or with conduplicate lateral pairs and flattened facial pairs. Branchlet-systems either flattened, with the pinnae in one plane, or arising at varying angles, with the pinnae in several planes. Cones large, usually ½ in. or more in diameter, ripening in the second year. Seeds, 6–20 on each scale.

For Descriptions of the Species, see Special Key.

1. *C. torulosa,* Don.—Himalayas and China.
2. *C. funebris,* Endlicher.—Weeping Cypress. China.
3. *C. cashmeriana,* Royle.—Kashmir Cypress. Himalayas.
4. *C. lusitanica,* Miller.—Mexican Cypress. Mexico.
5. *C. Benthami,* Endlicher.—Mexico.
6. *C. Duclouxiana,* Hickel.—China.
7. *C. Macnabiana,* Murray.—Macnab's Cypress. California.
8. *C. arizonica,* Greene.—Arizona Cypress. Mexico, Arizona.
9. *C. glabra,* Sudworth.—Central Arizona.
10. *C. sempervirens,* Linnaeus.—Mediterranean Cypress. Southern Europe.
11. *C. macrocarpa,* Hartweg.—Monterey Cypress. California.
12. *C. Goveniana,* Gordon.—Gowen Cypress. California.

II.—CHAMAECYPARIS.

Leaves entire in margin, the lateral pair conduplicate, the facial pair flattened. Cones small, less than ⅓ in. in diameter. Seeds, 1–5 on each scale. Branchlet-systems flattened, with the pinnae in one plane.

13. *C. obtusa,* Koch.—Hinoki Cypress. Japan.
14. *C. Lawsoniana,* Murray.—Lawson Cypress. North America.
15. *C. pisifera,* Koch.—Sawara Cypress. Japan.
16. *C. nootkatensis,* Don.—Yellow Cypress. Western North America.
17. *C. thyoides,* Linnaeus.—White Cypress. North America.
18. *C. formosensis,* A. Henry.—Formosan Cypress. Formosa.

22.—*THUYA.*

Trees with an erect leading shoot. *Branches* terminating in so-called "branchlet-systems," which are flattened in one plane, and 2-, 3-, or 4-pinnately divided, their primary and other axes being densely covered by the scale-like leaves, arranged in opposite decussate pairs. *Cones* solitary, more or less pendulous when ripe, oblong, about ½ in. long, with 5 or 6 pairs of scales, some fertile, the others sterile. Scales oval or spatulate, with a rounded apex, and with a small external process. Seeds, 2 or 3 on each fertile scale, up to ¼ in. long, surrounded by a narrow wing.

There are five species, of which only one, *T. plicata,* is suitable for planting as a forest tree in the British Isles. Three of the other species are cultivated for ornament. *Distribution*: North America, Japan, and China.

Thuya plicata will grow on almost any soil, and does well on wet, peaty, or shallow chalky soils. It may be planted pure, or in mixture with other species, such as larch. Thuya is an intense shade-bearer, and plantations must be kept dense to encourage self-pruning and to prevent the production of coarse, knotty timber. It may be used for underplanting larch or ash, and is useful for filling up wet patches in woods, or it may be planted as a hedge. In damp localities it is liable to attack by a fungus, *Keithia thujina,* which is a serious pest in seed-beds and in young plantations.

The wood is brown in colour, light, strong, durable, and is easily worked. It is used for telegraph poles, railway sleepers, building construction, and other purposes.

For Descriptions of the Species, see Special Key.

1. *T. plicata,* D. Don (*T. gigantea,* Nuttall).—Giant Thuya. Western North America.
2. *T. occidentalis,* Linnaeus.—Arbor-vitae. Eastern North America.
3. *T. japonica,* Maximowicz.—Japanese Thuya. Japan.
4. *T. sutchuenensis,* Franchet.—Chinese Thuya. Central China.
5. *T. koraiensis,* Nakai.—Korean Thuya. Korea.

23.—*BIOTA.* CHINESE ARBOR-VITAE.

A small tree, sometimes attaining 60 feet in height. *Branches* ascending, with the branchlets disposed in vertical planes at right angles to the stem of the tree. *Leaves* in opposite decussate pairs, scale-like in adult trees, with conduplicate lateral pairs and flattened facial pairs. Ultimate branchlets $\frac{1}{16}$ in. wide. *Cones* erect on the branchlets, ovoid, ½ in. in diameter, fleshy and bluish before ripening, dry and woody when mature, with three pairs of scales bearing hook-like processes. Seeds, 2 on each scale, large, ovoid, brown, wingless.

One species, *B. orientalis,* Endlicher (*Thuya orientalis,* Linnaeus) is known, a native of the mountains of northern and south-western China. Plate 13, fig. 42.

Biota is of no economic importance. It is hardy in the British Isles, and is commonly cultivated as an ornamental tree.

24.—*MICROBIOTA.*

A small shrub. *Branches* terminating in branchlet-systems, which are flattened in one plane. Ultimate branchlets equal-sided, slightly flattened, $\frac{1}{16}$ in. wide. *Leaves* in opposite decussate pairs, scale-like; appressed, rhombic-ovate; apex acuminate, with a mucronate point; dorsal surface convex, with an obscure glandular depression. *Cones* globose, $\frac{1}{8}$ in. in diameter, purple, with one unwinged seed.

One species is known, *M. decussata*, Komarov, occurring in Eastern Siberia. It is not yet introduced into cultivation. Plate 13, fig. 43.

Microbiota is of no economic value.

25.—*LIBOCEDRUS.*

Usually tall trees. *Branchlets* 3- or 4-pinnately divided, ultimate branchlets flattened or tetragonal. *Leaves* in opposite decussate pairs, scale-like, in most species with distinct stomatic hollows. *Cones* pendulous or erect, cylindrical, up to $\frac{3}{4}$ in. long, with four to six woody scales. Seeds with two lateral wings; one broad, oblique, nearly as long as the scale; the other short, rudimentary.

Nine species are known. They have all been introduced except *L. arfakensis*, *L. papuana*, and *L. austro-caledonica*. *Distribution*: North and South America, New Zealand, and New Caledonia.

None of the species of Libocedrus is of value for commercial planting in the British Isles. *L. decurrens* is perfectly hardy, and is cultivated as an ornamental tree. The other species are tender, and can only be grown out of doors in the milder parts of England and Ireland. They are of small economic importance in their native countries, the timber being used locally for general purposes. The wood is reddish-brown or brown in colour, with a fragrant odour, durable and easily worked.

The genus is divided into two sections:—

I.—Ultimate branchlets tetragonal, with leaves all alike and uniform in size. Branchlet-systems arising at varying angles, not flattened in one plane.

For Descriptions of the Species, see Special Key.

1. *L. tetragona*, Endlicher.—Chile.
2. *L. Bidwillii*, J. D. Hooker.—New Zealand.

II.—Ultimate branchlets flattened, with leaves of two kinds; lateral pairs conduplicate, facial pairs flattened. Branchlet-systems flattened, all the branchlets arising from the main axis in one plane.

3. *L. decurrens*, Torrey.—Incense Cedar. Oregon, California.
4. *L. macrolepis*, Bentham and Hooker.—China.

5. *L. chilensis,* Endlicher.—Chile.
6. *L. Doniana,* Endlicher.—New Zealand.
7. *L. papuana,* F. Mueller.—New Guinea.
8. *L. arfakensis,* Gibbs.—New Guinea.
9. *L. austro-caledonica,* Brongniart and Gris.—New Caledonia.

26.—*FOKIENIA.*

A tree up to 40 feet high. *Branches* terminating in branchlet-systems, which are flattened in one plane. Ultimate branchlets flattened, $\frac{1}{10}$ in. wide. *Leaves* in opposite decussate pairs, scale-like; lateral pair narrow, with short, blunt points, and with shallow white stomatic depressions on the lower surface; facial pair oblanceolate, the upper one with a shallow depression on the back, apex triangular, short-pointed. On young plants the leaves are larger, and are sharp-pointed. *Cones* globose, 1 in. in diameter, with 6–12 peltate woody scales. Seeds, 2 on each fertile scale, $\frac{1}{6}$ in. long, with 2 unequal wings.

One species, *F. Hodginsii,* A. Henry and Thomas, is known, a native of Fokien Province, China. Plate 13, fig. 46.

Fokienia is of no economic importance. It has been introduced and is hardy in the milder parts of England and Ireland, but is rare in cultivation.

27.—*THUJOPSIS.*

Large trees up to 100 feet high. *Branches* terminating in branchlet-systems, which are flattened in one plane. Ultimate branchlets flattened. *Leaves* in opposite decussate pairs, scale-like, with conduplicate lateral pairs, and flattened facial pairs. Lateral leaves wide-spreading; upper surface convex from side to side, dark shining green; lower surface concave, with white stomatic patches. Facial leaves oblanceolate; upper ones swollen towards the rounded apex, with a central ridge, which is often furrowed in the middle line; lower ones with a median ridge, and two white stomatic depressions. *Cones* globular, $\frac{1}{2}$–$\frac{3}{4}$ in. long, with 8 woody scales. Seeds, 3–5 on a scale, with one wing, which is not notched at the apex.

Two closely allied species are known, occurring in Japan.

For Descriptions of the Species, see Special Key.

1. *T. dolobrata,* Siebold and Zuccarini.—South Japan.
2. *T. Hondai,* A. Henry.—North Japan.

Thujopsis is an important forest tree in Japan, yielding durable timber, which is used for building construction, railway sleepers, and other purposes. The two species are hardy in the British Isles, and are in cultivation as ornamental trees and for hedges.

The wood is yellowish-white in colour, fine-grained, and easily worked.

CUPRESSUS, THUYA, BIOTA, MICROBIOTA, THUJOPSIS, LIBOCEDRUS, and FOKIENIA.

SPECIAL KEY.

I.—BRANCHLET-SYSTEMS FLATTENED, ALL THE BRANCHLETS ARISING FROM THE MAIN AXIS IN ONE PLANE.

A.—UNDER SURFACE OF THE FOLIAGE WITHOUT STOMATIC DEPRESSIONS.

(I).—ULTIMATE BRANCHLETS EQUAL-SIDED; LEAVES UNIFORM IN FOUR RANKS AND SIMILAR IN SHAPE.

1. *Cupressus torulosa,* Don. — Himalayan Cypress. Himalayas and China. Leaves appressed, ovate, obtuse at the apex, convex on the back, with an obscure glandular depression. Ultimate branchlets terete, $\frac{1}{24}$ in. in diameter, slightly curved. Plate 14, fig. 61. Cones $\frac{1}{2}$ in., globose or ellipsoid; scales, 8 or 10, external surface depressed, with a minute process. A tree up to 150 feet high in its native country, where it is an important forest tree. Cultivated for ornament.

2. *Microbiota decussata,* Komarov. — Eastern Siberia. Leaves appressed, rhombic-ovate, acuminate, apex mucronate; convex on the back, with an obscure glandular depression. Ultimate branchlets tetragonal, slightly flattened, $\frac{1}{16}$ in. wide, straight. Plate 13, fig. 43. Cones $\frac{1}{4}$ in., globose, purple. A small shrub. Not introduced into cultivation.

(II).—ULTIMATE BRANCHLETS FLATTENED; LEAVES DIMORPHIC, LATERAL PAIRS CONDUPLICATE, FACIAL PAIRS FLATTENED.

(a) **Tips of facial leaves projecting in advance of tips of lateral leaves.**

(*a*) *Under surface of the foliage snowy white.*

3. *Thuya koraiensis,* Nakai.—Korea. Leaves appressed; facial pair rhomboidal, obtuse at the apex, with an oval glandular depression on the back. Ultimate branchlets $\frac{1}{10}$ in. wide. Cones $\frac{3}{8}$ in., oblong, with 6 or 8 pairs of thin oval or spatulate scales. A small tree. Cultivated for ornament.

(*b*) *Under surface of the foliage with X-shaped, clearly defined white markings.*

4. *Cupressus obtusa,* Koch. — Hinoki Cypress. Japan. Leaves appressed; facial pair rhomboidal, often keeled on the back, with a triangular scarcely acute apex. Ultimate branchlets $\frac{1}{15}$ in. wide. Cones $\frac{1}{3}$ in., globose, orange-brown; scales, 8 or 10, outer surface depressed, with a minute ridge. A tree up to 100 feet high in its native country, where it is an important forest tree. Cultivated for ornament.

(*c*) *Under surface of the foliage green, or with X-shaped, ill-defined white markings.*

5. *Cupressus Lawsoniana,* Murray. — Lawson Cypress. Western North America. Leaves appressed; facial pair rhomboidal, often marked with a glan-

dular depression on the back, with an acute minutely mucronate apex. Plate 13, fig. 40. Cones, $\frac{1}{3}$ in., globose, glaucous; scales, 8, external surface depressed, with a ridge-like process. A valuable timber tree in Oregon, attaining a height of 200 feet. It is perfectly hardy, and thrives in all parts of the British Isles, where it is usually grown for ornament, but occasionally planted as a forest tree. See note under Cupressus (Genus).

(*d*) *Foliage glaucous blue.*

6. *Cupressus cashmeriana,* Royle.—Kashmir Cypress. Himalayas. Leaves spreading, acuminate, with a mucronate apex; facial pair flattened, with a longitudinal furrow on the back. Ultimate branchlets $\frac{1}{30}$ in. wide. Plate 14, fig. 62. Cones, $\frac{1}{2}$ in., ellipsoidal; scales, 10, outer surface depressed, with a minute reflexed process. A tree up to 60 feet high. Known only in cultivation. Rare as an ornamental tree.

(*e*) *Under surface of the foliage green, without whitish lines or streaks.*

7. *Cupressus funebris,* Endlicher. — Weeping Cypress. China. Foliage greyish green. Leaves appressed, but with the mucronate apex free and slightly spreading; facial pair ovate, keeled or with a median furrow. Ultimate branchlets terete, $\frac{1}{20}$ in. wide. Cones, $\frac{1}{3}$ in., globose; scales, 8, with a minute process. A tree up to 70 feet high. Cultivated for ornament.

8. *Cupressus Benthami,* Endlicher (*C. lusitanica,* Miller, var. *Benthami,* Carrière).—Mexico. Foliage dark green. Main axis of the branchlet bright red in the second year. Leaves appressed, but with free mucronate apex; facial pair rhomboidal, with a depressed circular gland. Ultimate branchlets tetragonal, $\frac{1}{16}$ in. wide. Cones glaucous in the first year, $\frac{1}{2}$ in., globose; scales, 8, with a prominent process. A tree up to 100 feet high. Cultivated for ornament.

(b) **Tips of facial leaves level with tips of lateral leaves.**

(*a*) *Under surface of the foliage with white patches.*

9. *Cupressus pisifera,* Koch.—Sawara Cypress. Japan. Leaves appressed, but with their mucronate apices free and slightly spreading; facial pair ovate-acuminate, often ridged on the back, with an obscure gland. Ultimate branchlets $\frac{1}{16}$ in. wide. Cones, $\frac{1}{4}$ in., globose, dark brown; scales, 10, wrinkled and deeply depressed in the centre. A tree up to 90 feet high. Cultivated for ornament.

10. *Thuya plicata,* D. Don (*T. gigantea,* Nuttall).—Giant Thuya. Western North America. Leaves appressed, but with apex free; lateral pair ending in long fine points, which are parallel to the axis; facial pair rhomboidal, often with a raised gland. Ultimate branchlets $\frac{1}{12}$ in. wide. Plate 13, fig. 41. Cones, $\frac{1}{2}$ in., oblong, with thin oval scales. Next to Douglas Fir, this is the most important tree in Oregon, Washington, and British Columbia, where it attains

a height of 200 feet. It is very vigorous in growth in the British Isles, and is a valuable commercial species. See note under Thuya (Genus).

11. *Thuya japonica,* Maximowicz. — Japanese Thuya. Central Japan. Leaves closely appressed, but with free apex; lateral pair with short thick triangular points; facial pair rhomboidal, keeled on the back, with an obtuse apex; non-glandular. Ultimate branchlets $\frac{1}{10}$ in. wide. Cones $\frac{1}{2}$ in., oblong, with thin oval scales. A tree up to 40 feet. Cultivated for ornament.

(*b*) *Under surface of the foliage green, without white markings.*

(i) *Upper surface of the foliage with circular elevated glands.*

12. *Thuya occidentalis,* Linnaeus.—American Arbor-vitae. Eastern North America. Leaves appressed, but with free apex; lateral pair ending in long points, which are parallel to the axis; facial pair rhomboidal, acute. Ultimate branchlets $\frac{1}{10}$ in. wide. Cones, $\frac{1}{2}$ in., oblong, with thin oval scales. A tree up to 60 feet high. Of no value for commercial planting. Cultivated for ornament.

13. *Cupressus thyoides,* Linnaeus.—White Cypress. North America. Leaves appressed; lateral pair with mucronate, slightly spreading apices; facial pair ovate-triangular, acute, flattened or keeled. Ultimate branchlets $\frac{1}{30}$ in. wide. Cones, $\frac{1}{4}$ in., globose, bluish purple, and covered with a glaucous bloom; scales, 6, with a reflexed central process. A useful timber tree in its native country, where it attains a height of 80 feet. Cultivated in Europe for ornament.

(ii) *Upper surface of the foliage with oval depressed glands.*

14. *Biota orientalis,* Endlicher (*Thuya orientalis,* Linnæus).—Chinese Arbor-vitae. China. Branches ascending with the branchlets disposed in vertical radial planes. Leaves short, $\frac{1}{16}$ in., appressed, but with free-spreading apex; lateral pair with triangular points; facial pair ovate-triangular, with an acute apex. Ultimate branchlets $\frac{1}{16}$ in. wide. Plate 13, fig. 42. Cones, $\frac{1}{2}$ in., ovoid, bluish, with 6 scales, bearing hooked processes. A tree up to 40 feet high. Cultivated for ornament.

15. *Libocedrus decurrens,* Torrey.—Incense Cedar. Oregon and California. Leaves, $\frac{1}{8}$ in. long, appressed, but with apices free, and tipped with long fine cartilaginous points; lateral pair covering only the margins of the facial pair. Ultimate branchlets $\frac{1}{12}$ in. wide. Plate 13, fig. 45. Cones cylindrical, $\frac{3}{4}$ in. long, with 6 scales, upper pair with 3 minute spines. A tree up to 180 feet. Cultivated for ornament.

(iii) *Leaves non-glandular; facial leaves with a median ridge.*

16. *Cupressus nootkatensis,* Don.—Yellow Cypress. Western North America. Branchlets in the upper part of the tree pendulous, in vertical radial planes. Leaves appressed, but with free and spreading apex; lateral pair acute, and minutely mucronate; facial pair ovate-triangular, often with a longitudinal

furrow, acute or mucronate. Ultimate branchlets $\frac{1}{12}$ in. wide. Plate 14, fig. 63. Cones, $\frac{1}{3}$ in., globose, reddish; scales, 4 or 6, with a prominent pointed process. A tree up to 120 feet high; valuable for timber in its native country. Usually cultivated for ornament, but may be planted as a forest tree.

17. *Cupressus formosensis,* Henry.—Formosan Cypress. Formosa. Leaves closely appressed; lateral pair with an incurved usually mucronate apex; facial pair rhomboidal, apex acute or mucronate. Ultimate branchlets $\frac{1}{16}$ in. wide. Cones, $\frac{1}{3}$ in., ellipsoid; scales, 10, wrinkled, brownish, depressed in the centre with a quadrangular process. A tree up to 80 feet high; valuable for timber in its native country. Rare in cultivation.

18. *Thuya sutchuenensis,* Franchet. — China. Leaves closely appressed; lateral pair with a blunt incurved apex; facial pair rhomboidal, obtuse at the apex. A small tree. Not introduced.

B.—UNDER SURFACE OF THE FOLIAGE WITH STOMATIC DEPRESSIONS, WHITE PATCHES SUNK IN HOLLOWS IN THE LEAVES.

(I) Lateral and facial leaves equal in length.

(a) Leaves appressed.

18 A. *Thuya koraiensis,* Nakai.—Stomatic depressions indistinct. See No. 3.

18 B. *Cupressus pisifera,* Koch.—Stomatic depressions indistinct. See No. 9.

19. *Libocedrus macrolepis,* Bentham and Hooker. — China. Ultimate branchlets very thin and flat, $\frac{1}{6}$ in. wide. Lateral leaves narrow, with a sharp-pointed acuminate apex; median leaves oblanceolate, keeled on the back, with a longitudinal furrow; apex triangular, sharp-pointed. Cones, $\frac{3}{4}$ in. long, tetragonal, with 3 pairs of scales. A tree up to 100 feet high. Hardy in the milder parts of England and Ireland, but rare in cultivation.

20. *Fokienia Hodginsii,* Henry and Thomas.—China. Ultimate branchlets flattened, $\frac{1}{16}$ in. wide. Lateral leaves narrow, with short blunt points. Facial leaves oblanceolate, the upper one with a longitudinal furrow on the back; apex triangular, short-pointed. Ultimate branchlets on young plants $\frac{1}{4}$ in. wide, with sharp-pointed leaves, the lateral pair much longer than the median pair. Plate 13, fig. 46. *A.* Adult foliage. *B.* Juvenile foliage. Cones globose, 1 in.; scales, 12–16, with a central process. A tree up to 40 feet high. Rare in cultivation.

(b) Leaves spreading.

21. *Thujopsis dolabrata,* Siebold and Zuccarini. — South Japan. Ultimate branchlets up to $\frac{1}{5}$ in. wide. Lateral leaves spatulate, with an acute incurved apex. Facial leaves oblanceolate, upper ones swollen towards the rounded apex, with a central ridge often hollowed in the middle line. Plate 13, fig. 44. Cones globose, $\frac{3}{4}$ in., with 8 scales bearing prominent processes. Up to 50 feet high in its native country, where it is a shrub or small tree. Cultivated as an ornamental tree and planted as a hedge.

22. *Thujopsis Hondai,* A. Henry.—Northern Japan. Resembles No. 21, but has smaller leaves. Ultimate branchlets $\frac{1}{8}$ in. wide. Cone-scales without a process. A tree up to 100 feet high. Rare in cultivation.

(II) Lateral leaves much longer than the facial leaves.

(a) Lateral leaves wide-spreading.

23. *Libocedrus chilensis,* Endlicher.—Chile. Lateral leaves $\frac{1}{3}$ in. long, free for one-third their length. Facial leaves minute, rounded or acute at the apex, with a conspicuous elevated gland. Cones cylindrical, $\frac{1}{2}$ in. long; scales 4, with a minute projecting point below the apex. A tree up to 50 feet high. Rare in cultivation.

(b) Lateral leaves appressed.

24. *Libocedrus Doniana,* Endlicher. — New Zealand. Lateral leaves $\frac{3}{16}$ in. long, free at the acute mucronate apex. Facial leaves rhomboidal, with a median ridge and an inconspicuous gland; apex acute, mucronate. Cones cylindrical, $\frac{1}{2}$ in. long; scales 4, with a prominent spine in the centre of the back. A tree up to 100 feet high. Rare in cultivation.

II.—BRANCHLET-SYSTEMS NOT FLATTENED, THE BRANCHLETS ARISING AT VARYING ANGLES AND SPREADING RADIALLY FROM THE MAIN AXIS.

A.—Leaves with a conspicuous circular pit, exuding white resin. Leaves closely appressed.

25. *Cupressus Macnabiana,* Murray.—Macnab's Cypress. California. Ultimate branchlets compressed, $\frac{1}{24}$ in. wide. Leaves ovate, obtuse, not glaucous. Cones globose, $\frac{1}{2}$–$\frac{3}{4}$ in., reddish-brown, often glaucous; scales 6, with a prominent process. A small tree, occasionally attaining 40 feet. Rare in cultivation.

26. *Cupressus glabra,* Sudworth.—Arizona Cypress. Arizona and N. Mexico. Ultimate branchlets tetragonal, equal-sided, $\frac{1}{20}$ in. in diameter. Leaves rhomboidal, acute or acuminate, grey, sometimes glaucous. A tree up to 60 feet high. Common in cultivation under the name of *C. arizonica.* The true *C. arizonica,* Greene, has leaves without glands, and is very rare in cultivation.

B.—Leaves with a depressed circular gland.

27. *Cupressus lusitanica,* Miller. — Mexican Cypress. "Cedar of Goa," Mexico. Leaves ovate-acuminate, often mucronate, convex from side to side, slightly free at the tips. Ultimate branchlets tetragonal, slightly compressed, $\frac{1}{16}$ in. wide, $\frac{1}{20}$ in. thick. Main axis of branchlet usually bright red in the second year. Cones remarkably glaucous in the first year, globose, $\frac{1}{2}$ in.; scales 8, with a prominent process. A tree up to 80 feet high. Cultivated for ornament.

C.—Leaves not conspicuously glandular. Ultimate branchlets tetragonal, equal-sided.

(I) Leaves closely appressed, usually with a median longitudinal furrow on the back.

28. *Cupressus sempervirens*, Linnaeus.—Mediterranean Cypress. Asia Minor, Greece, Levant, Persia. Ultimate branchlets $\frac{1}{28}$ in. in diameter. Leaves rhomboidal, obtuse, closely appressed at the apex. Plate 14, fig. 60. Cones subglobose or ovoid, 1–1¼ in., pale brown or greyish; scales 10–14, either with a central pit overhung by a minute process, or rising to a quadrangular process. A tree up to 100 feet high. Cultivated for ornament.

29. *Cupressus macrocarpa*, Hartweg.—Monterey Cypress. California. Ultimate branchlets $\frac{1}{20}$ in. in diameter. Leaves ovate, obtuse, swollen towards the slightly raised apex. Plate 13, fig. 47. Cones ellipsoidal, 1–1¼ in. long, shining reddish-brown; scales 8–14, with a central depression overhung by a thin ridge-like process. A tree up to 80 feet high. It grows at a rapid rate in the British Isles, and produces a large volume of strong durable timber. It does not stand cold winds and suffers from spring frost, and only succeeds in districts near the sea-coast and at low elevations in a mild climate. It may be planted in shelter-belts or hedges.

30. *Cupressus Goveniana*, Gordon.—Gowen's Cypress. California. Ultimate branchlets $\frac{1}{24}$ in. in diameter. Leaves ovate, swollen near the apex, which is acute and often mucronate. Cones globose, ½–¾ in., shining dark brown; scales 6–10, projecting in the centre, with a prominent process. A tree up to 50 feet high. Cultivated for ornament.

31. *Cupressus Duclouxiana*, Hickel.—Ducloux's Cypress. China. Ultimate branchlets $\frac{1}{35}$ in. in diameter, glaucous. Leaves ovate, slightly swollen near the apex, which is acute and often mucronate. Cones globose, ¾–1 in.; scales 8, with a prominent process. Rare in cultivation.

(II) Leaves not closely appressed, but with the apex free and spreading, and with a keel and two lateral furrows on the back.

32. *Libocedrus tetragona*, Endlicher.—Chile. Leaves wide-spreading, large, $\frac{1}{10}$ in. long, acute or rounded at the incurved apex; ventral surface concave, with a white stomatic band. Plate 14, fig. 52. Cones cylindrical, ½ in. long; scales 4, minutely pubescent on the margin, with an erect incurved spine. A tree up to 150 feet high. Rare in cultivation.

33. *Libocedrus Bidwillii*, J. D. Hooker.—New Zealand. Leaves loosely appressed, small, $\frac{1}{16}$ in. long, ovate, acute at the incurved apex. Ultimate branchlets slightly compressed. Cones ⅓ in. long, cylindrical; scales 4, with an erect incurved spine. A tree up to 60 feet high. Rare in cultivation.

28.—*JUNIPERUS.* JUNIPERS.

Trees or shrubs. *Leaves* on young plants always acicular, usually in whorls of threes; on adult trees, either acicular or appressed and scale-like, different in the sections of the genus. *Fruit,* a succulent berry-like indehiscent strobile, composed of three to eight fleshy scales, united together; ripening in the first, second, or rarely in the third year. Seeds, one to twelve, variable in shape.

About fifty-six species are known, none of which is of value for forestry purposes in the British Isles. *Distribution*: Arctic Circle to Mexico, West Indies, Azores and Canary Islands, Northern Africa, Abyssinia, the mountains of East Tropical Africa, Himalayas, China, Japan, and Formosa.

Some of the Junipers are of economic importance in their native countries, yielding small timber of good quality, used locally for furniture making and general purposes. The wood of *J. virginiana,* known as the "Pencil Cedar," is the most valuable known wood in the manufacture of lead pencils. The wood is reddish, or reddish brown, fine-grained, very durable, and easily worked.

I.—LEAVES ALWAYS ACICULAR, SPREADING IN WHORLS OF THREES.

A.—Leaves jointed at the base; not decurrent on the branchlets.

Section Oxycedrus.

Leaves always spreading (never appressed), linear, rigid, convex, and green beneath, whitened above with one or two stomatic bands, entire in margin, without glands; branchlets glabrous, and triangular in section.

(I) Leaves with one white stomatic band above.

1. *J. communis,* Linnaeus.—Common Juniper. Europe, Extratropical Asia, N. America. Leaves $\frac{2}{5}$–$\frac{3}{5}$ in. long, slightly concave above, no trace of a green midrib being present, except in rare cases near the base. In var. *nana,* leaves shorter, $\frac{1}{6}$–$\frac{1}{3}$ in. long. Plate 14, fig. 54. A shrub or tree. Common wild and in cultivation.

2. *J. rigida,* Siebold and Zuccarini.—Japan. Leaves $\frac{1}{2}$–$\frac{3}{4}$ in. long, very slender, deeply concave above, with the margins inflexed, forming a narrow median groove. A tree up to 30 feet high. In cultivation.

(II) Leaves with two white stomatic bands above.

(a) Shrubs, with leaves spreading horizontally outwards; branchlets usually not pendulous.

3. *J. Oxycedrus,* Linnaeus. — Mediterranean Region, Caucasus, Persia, Madeira Islands. Leaves $\frac{1}{2}$–$\frac{3}{4}$ in. long, gradually tapering from the middle to the sharp-pointed acuminate apex; upper surface with a conspicuous midrib, about half the width of the white bands, which are equal in width to the marginal green bands. In cultivation.

4. *J. macrocarpa,* Sibthorp and Smith. — Mediterranean Region. Leaves $\frac{3}{4}$–1 in. long, tapering from the base to the sharp-pointed acuminate apex;

upper surface with a conspicuous midrib, less than half the width of the white bands, which are broader than the marginal green bands. Rare in cultivation.

5. *J. brevifolia,* Antoine.—Azores. Leaves oval-linear, very short, ¼–⅓ in. long; apex rounded or acute, and not acuminate; upper surface with a conspicuous midrib and white bands, broader than the green bands. Not yet introduced.

(*b*) *Trees, with leaves directed forwards towards the apices of the pendulous branchlets.*

6. *J. Cedrus,* Webb and Berthelot.—Canary Islands. Leaves ½–¾ in. long, with a conspicuous midrib above, about half the width of the white bands, which equal in width the marginal green bands. Up to 80 feet high. In cultivation.

7. *J. formosana,* Hayata.—China, Formosa. Leaves ½–¾ in. long, upper surface with a midrib much narrower than the white bands, which are broader than the marginal green bands. Up to 40 feet high. Rare in cultivation.

B.—Leaves jointed at the base; decurrent on the branchlets. Section Caryocedrus.

Leaves similar to those in section Oxycedrus, but differing in their attachment to the branchlets.

8. *J. drupacea,* Labillardière.—Greece, Asia Minor, Syria. Leaves ½–⅞ in. long, widely spreading, very rigid, sharp-pointed; upper surface with a broad green midrib, deeply furrowed near the base, and two white bands, which are much broader than the marginal green bands. Plate 14, fig. 64. A tree up to 60 feet high. In cultivation.

C.—Leaves not jointed near the base.

Section Sabina, in part.

Leaves linear-lanceolate, sharp-pointed, nearly appressed or more or less spreading, whitened on the ventral surface. Usually in whorls of threes, but sometimes in opposite pairs.

9. *J. recurva,* Buchanan-Hamilton. — Himalayas. A tree with curved branchlets. Leaves loosely appressed, greyish-green on the dorsal surface, which is channelled in the middle line near the base. Plate 14, fig. 65. Up to 30 feet high. Rare in cultivation.

10. *J. squamata,* Buchanan-Hamilton. — Afghanistan, Himalayas, China, Japan, Formosa. A prostrate shrub. Leaves appressed or spreading, broader and shorter than in *J. recurva,* green on the dorsal surface, which is channelled from the base to near the apex. Occasionally cultivated.

10a. *J. procumbens,* Siebold. — Japan. Similar to *J. squamata,* but with larger leaves, which, like the branchlets, are glaucous in tint.

II.—LEAVES SCALE-LIKE, IN OPPOSITE DECUSSATE PAIRS; CLOSELY APPRESSED, IMBRICATE.

SECTION SABINA, in part.

Acicular foliage occurs on occasional branches of the trees in most species.

A.—LEAVES DENTICULATE IN MARGIN.

(I) Acicular leaves in whorls of threes.

11. *J. Wallichiana,* J. D. Hooker.—Himalayas. Ultimate branchlets $\frac{1}{16}$ in. in diameter; scale-like leaves closely appressed, ovate, acute, with a conspicuous linear furrow on the back from base to apex. Acicular foliage usually present, similarly furrowed on the back. Fruit blue, with one very large seed. A tree up to 60 feet high. Rare in cultivation.

12. *J. phoenicea,* Linnaeus. — Mediterranean region, Crimea, Canary and Madeira Islands. Ultimate branchlets $\frac{1}{25}$ in. in diameter; scale-like leaves closely appressed, ovate, blunt, with an inconspicuous oval depression on the back. Acicular foliage rare on adult trees. Fruit yellow or reddish-brown, with fibrous yellow flesh, and three to nine seeds. A shrub or tree up to 20 feet high. Rare in cultivation.

13. *J. flaccida,* Schlechtendal.—Texas, Mexico. A tree with long pendulous branchlets. Scale-like leaves, ovate-lanceolate, slightly spreading, $\frac{1}{12}$ in. long, sharp-pointed, with a linear sunken gland, exuding resin. Acicular foliage usually present, similarly glandular. Fruit reddish-brown, with six to twelve seeds. A tree up to 40 feet high. Rare in cultivation.

14. *J. pachyphlaea,* Torrey.—Arizona, Texas, New Mexico, Mexico. Trees with thick bark, divided into small square scaly plates, unique in the genus. Ultimate branchlets $\frac{1}{25}$ in. in diameter; scale-like leaves, appressed, ovate, with a depressed oval gland, often exuding resin. Acicular leaves often present. Fruit reddish-brown, tuberculate, with four seeds. A tree up to 60 feet high. Rare in cultivation.

(II) Acicular leaves in opposite pairs.

15. *J. thurifera,* Linnaeus. — Spain, Portugal, Southern France, Sardinia, Morocco, and Algeria. Ultimate branchlets $\frac{1}{20}$ in. in diameter; scale-like leaves ovate, appressed, but free at their acute or acuminate tips, with a conspicuous glandular depression on the back. Acicular foliage often present. Fruit blue, with two to four seeds. A tree up to 40 feet high. In cultivation.

B.—LEAVES ENTIRE IN MARGIN.

(I) Acicular leaves in whorls of threes.

16. *J. chinensis,* Linnaeus.—China and Japan. Ultimate branchlets $\frac{1}{25}$ in. in diameter; marked with white crosses, due to the pale margins of the appressed leaves. Scale-like leaves rhombic, obtuse, with an inconspicuous dorsal gland. Acicular foliage usually present. Plate 14, fig. 51. Fruit brown, covered with

a white mealy bloom, sub-globose, widest and depressed at the summit, with usually two or three seeds. A tree up to 60 feet high. Common in cultivation.

17. *J. bermudiana,* Linnaeus. — Bermuda. Ultimate branchlets $\frac{1}{20}$ in. in diameter; leaves closely appressed, ovate, obtuse at the incurved apex, with an inconspicuous dorsal furrow. Acicular leaves usually present, furrowed on the back. Fruit dark blue, covered with a glaucous bloom, with two or three seeds. A tree up to 50 feet high. Rare in cultivation.

18. *J. procera,* Hochstetter.—Abyssinia, Kenya, Arabia. Ultimate branchlets very fine, $\frac{1}{30}$ in. in diameter; leaves closely appressed, ovate-rhombic, acute at the incurved apex, with a dorsal furrow. Acicular foliage rarely present. Fruit $\frac{1}{4}$ in. in diameter, bluish, covered with a white mealy bloom, with two or three seeds. A tree up to 80 feet high. Rare in cultivation.

(II) Acicular leaves in opposite pairs.

19. *J. virginiana,* Linnaeus.—North America. Ultimate branchlets very slender, $\frac{1}{30}$ in. in diameter; leaves closely appressed, acute or acuminate, with often a small oval depression on the back. Plate 14, fig. 66. Acicular foliage usually present. Fruit bluish, $\frac{1}{4}$ in. in diameter, with one or two seeds. A tree up to 100 feet high in its native country, where the timber is used for the manufacture of lead-pencils. In cultivation.

20. *J. Sabina,* Linnaeus.—Savin Juniper. Europe, Caucasus, North America. Foliage when bruised with a strong disagreeable odour. Ultimate branchlets very slender, $\frac{1}{30}$ in. in diameter; leaves appressed, ovate, acute or acuminate, with a conspicuous depressed dorsal resin-gland. Acicular foliage often present. Fruit bluish, $\frac{1}{5}$ in. in diameter, with usually two seeds. A shrub up to 15 feet high. Common in cultivation.

21. *J. excelsa,* Bieberstein.—Balkan States, Crimea, Syria, Asia Minor, Caucasus. Ultimate branchlets very slender, $\frac{1}{30}$ in. in diameter; leaves appressed, ovate-rhombic, acute or obtuse, marked on the back with a depressed gland. Acicular foliage rarely present. Fruit dark purplish brown, $\frac{1}{2}$ in. in diameter, with about six seeds. A tree up to 70 feet high. In cultivation.

29.—*FITZROYA.*

A tree up to 100 feet high. *Leaves* in whorls of threes, decurrent on the branchlets; free part spreading, spatulate, incurved at the rounded apex, about $\frac{1}{5}$ in. long; upper surface concave, with two narrow white stomatic depressions; lower surface convex, with a raised midrib and two narrow white stomatic bands. *Cones* sub-globose, about $\frac{1}{3}$ in. in diameter, with six woody scales, ripening in the first year. Seeds, one on each fertile scale, with two wings.

Only one species is known, *F. patagonica,* J. D. Hooker—a native of Chile and Patagonia, where it is called "Alerce." In cultivation as an ornamental tree. Plate 14, fig. 53.

The timber is of good quality, and is used locally for furniture manufacture, cooperage, shingles, and other purposes.

30.—*DISELMA.*

A bush or a small tree up to 20 feet high. *Leaves* in opposite decussate pairs, scale-like, rhomboidal, densely imbricate; apex acuminate, incurved. Ultimate branchlets tetragonal, equal-sided $\frac{1}{2}\frac{1}{5}$ in. in diameter. Leaves sometimes in whorls of threes. *Cones* small, with two pairs of woody scales, the upper pair with two three-winged seeds.

One species is known, *D. Archeri,* J. D. Hooker—a native of Tasmania. Plate 14, fig. 50. It is not yet introduced, and is of no economic value.

31.—*CALLITRIS.* THE CYPRESS PINES OF AUSTRALIA.

Usually large trees. *Leaves* in whorls of threes, scale-like, almost entirely decurrent, only a small triangular portion at the upper end being free, and either incurved or appressed. Leaves on young plants linear, slightly decurrent. Ultimate branchlets of adult trees terete. *Cones* globose, ovoid or conical, up to $1\frac{1}{4}$ in. long, with six or eight unequal woody scales. Seeds, 2–9 on each scale, with two or three wings.

Twenty-one species have been described, occurring in Australia, Tasmania, and New Caledonia, where they are valuable timber trees. Their timber is said to resist the ravages of white ants. The wood is hard, close-grained, and durable. It is used for building construction, furniture making, and general purposes.

The genus is only hardy in very mild localities in England and Ireland.

1. *C. oblonga,* Richard. — Ultimate branchlets triangular. Apex of leaves acute. Plate 14, fig. 55. Cones conical, 1 in. long, $\frac{3}{4}$ in. in diameter near the base, with smooth scales. A bush or tree up to 25 feet high. Rare in cultivation.

2. *C. robusta,* R. Brown. — Ultimate branchlets terete. Apex of leaves blunt. Cones ovoid, $\frac{3}{4}$ in. in diameter, with tuberculate scales. A tree up to 100 feet high. Rare in cultivation.

3. *C. rhomboidea,* R. Brown. — Ultimate branchlets triangular. Apex of leaves acuminate. Cones globose, up to $\frac{3}{4}$ in. in diameter; scales smooth, with a dorsal process. Cones not in dense clusters. A tree up to 40 feet high. Rare in cultivation.

4. *C. tasmanica,* Baker and Smith.—Ultimate branchlets triangular. Apex of leaves acute or acuminate. Cones globose, up to $\frac{3}{4}$ in. in diameter; scales smooth, with a dorsal process. Cones in dense clusters.

5. *C. glauca,* R. Brown. — Ultimate branchlets terete, glaucous. Apex of leaves acute. Cones globose, $\frac{3}{4}$ in. in diameter, with tuberculate scales. A tree up to 100 feet high. Not introduced.

6. *C. verrucosa,* R. Brown. — Ultimate branchlets terete. Apex of leaves rounded or acute. Cones ovoid, $\frac{3}{4}$ in. in diameter, with tuberculate scales. A tree up to 30 feet high. Not introduced.

32.—*ACTINOSTROBUS.*

Shrubs up to 8 feet high. *Leaves* in whorls of threes, scale-like, decurrent for half their length, with a free triangular apex. Ultimate branchlets terete. *Cones* globose or ovoid, up to $\frac{3}{4}$ in. in diameter, with 6 equal woody scales, attached to a short central axis. Seeds triangular, one or two on each scale, with three wings.

Two species are known, natives of Western Australia, and of no economic importance.

1. *A. pyramidalis,* Miquel.—Leaves $\frac{1}{8}$ in. long, apex triangular and slightly spreading. Plate 14, fig. 56A. Cone scales with a triangular apex. Rare in cultivation.

2. *A. acuminatus,* Parlatore. — Leaves $\frac{1}{10}$ in. long, apex triangular, more spreading than in *A. pyramidalis.* Plate 14, fig. 56B. Cone scales with a narrow reflexed apex. Not introduced.

33.—*WIDDRINGTONIA.* CYPRESS PINES OF SOUTH AFRICA.

Trees or shrubs. *Leaves* in opposite decussate pairs on the ultimate branchlets, spirally arranged on the main axis of the branches; scale-like, non-imbricate, dorsal surface angular or convex from side to side. Ultimate branchlets tetragonal, equal-sided, up to $\frac{1}{16}$ in. in diameter. Juvenile leaves linear, in spiral order. *Cones* ovoid or globose, up to $\frac{3}{4}$ in. in diameter; scales 4, thick, woody, with a truncate apex. Seeds numerous, with two wings.

Five species are known, occurring in South Africa.

W. juniperoides, W. Schwarzii, and *W. Whytei* are important economically in South Africa, where the timber is used for furniture manufacture and the indoor finish of houses. The wood is moderately hard, is easily worked, and is free from insect attack.

1. *W. Schwarzii,* Marloth.—Cape Province. Leaves hexagonal, closely appressed at the acute apex. Plate 13, fig. 48. Cone-scales tuberculate. A tree up to 80 feet high.

2. *W. dracomontana,* Stapf.—Natal. Leaves rhombic-ovoid, closely appressed, but free and often slightly spreading at the acute apex. Cone-scales roughened. A tree up to 40 feet high.

3. *W. juniperoides,* Endlicher. — Cedarberg Mountains. Leaves rhombic-ovate, appressed at the rounded or acute apex. Cone-scales tuberculate, with a prominent process. A tree up to 60 feet high.

4. *W. cupressoides,* Endlicher.—Table Mountain Range and Natal. Leaves ovate-acuminate, appressed at the acute apex. Cone-scales smooth. A shrub up to 12 feet high.

5. *W. Whytei,* Rendle.—Transvaal. Leaves rhombic, free and incurved at the acute apex. Cone-scales tuberculate, with a prominent process. A tree up to 140 feet high.

34.—*TETRACLINIS.*

A tree up to 50 feet high. *Branches* terminating in branchlet-systems, which are flattened in one plane. *Leaves* in whorls of fours, scale-like, decurrent, with the apex free and spreading, the lateral pair slightly larger than and partly covering the facial pair. On young plants, in opposite decussate pairs, linear, up to $\frac{1}{4}$ in. long. *Cones* globose, up to $\frac{1}{2}$ in. in diameter; scales 4, thin, woody, with an obtuse apex and a small dorsal spine. Seeds with two wings.

Only one species is known, *T. articulata,* Masters, a native of Morocco, Algeria, and Tunis. It is hardy in the milder parts of the British Isles, but is rare in cultivation. Plate 14, fig. 57.

The wood of Tetraclinis is short-grained and hard. It is used for furniture manufacture and indoor work.

35.—*CALLITROPSIS.*

A tree up to 30 feet high. *Leaves* in whorls of fours, spreading, rigid, trigonous, broad at the base, gradually narrowing to the sharp-pointed apex. Ultimate branchlets terete, $\frac{1}{4}$ in. in diameter, with eight conspicuous rows of leaves. *Cones* cylindrical, $\frac{1}{2}$ in. long and $\frac{1}{4}$ in. in diameter, with 8 loosely imbricated scales in two whorls of four each. Seeds, 8 in a cone, inconspicuously winged.

Only one species, *C. araucarioides,* Compton, is known, a native of New Caledonia. It is not yet introduced, and is of no economic value. Plate 14, fig. 58.

TAXACEAE.

36.—*TAXUS.* YEWS.

Shrubs or small trees. *Leaves* spirally arranged, usually pectinate in two sets, spreading in one plane, linear, without a resin-canal; upper surface dark green, with a midrib; lower surface pale green, with inconspicuous stomatic lines

on each side of the midrib. *Fruit* a red fleshy glutinous aril, open at the top, containing a single seed; ripening in the first year.

Seven distinct species have been described. These are closely allied, and have been treated as geographical races of one species, the common European Yew. Widely spread in North America, Europe, Algeria, and Asia.

Yews have no value for commercial planting, but are commonly cultivated as ornamental trees and as hedges. The foliage is poisonous to farm animals, and trees should be securely fenced from stock. The wood is reddish-brown in colour, strong, hard, heavy, and close-grained. It is very durable, and is suitable for all kinds of outdoor work. It takes a good polish, and is used for furniture, panelling, parquet-flooring, and turnery.

1. *T. baccata,* Linnaeus.—Common Yew. Europe. Leaves falcate, apex acute or acuminate, with a cartilaginous mucro; midrib only slightly prominent above. Buds ovoid or globose, with closely imbricated brownish rounded scales, usually not keeled. Plate 10, fig. 29. A tree up to 90 feet high. One of the three conifers indigenous in the British Isles. Common in cultivation.

1A. *T. baccata,* var. *fastigiata,* Loudon. — Irish Yew, Florencecourt Yew. Leaves always spreading radially, dark green and shining. A tree or shrub, columnar and compact in habit, all the branches being directed vertically upwards. Common in cultivation.

2. *T. cuspidata,* Siebold and Zuccarini. — Japanese Yew. Japan. Leaves straight, scarcely falcate, midrib prominent above, apex mucronate. Buds oblong, composed of somewhat loosely imbricated scales, which are ovate, acute, and keeled. In cultivated specimens the under surface of the leaves is yellow in colour. A tree or shrub. Rare in cultivation.

3. *T. chinensis,* Pilger.—Chinese Yew. China. Leaves short, rigid; midrib not prominent above; apex rounded, mucronate. Buds ovoid, brownish, with densely imbricated scales, which are ovate, obtuse, and not keeled. A tree up to 50 feet high. In cultivation.

4. *T. canadensis,* Marshall.—Canadian Yew. Eastern North America. Leaves narrow, falcate; midrib slightly prominent above; apex mucronate. Buds globose, small, with somewhat loosely imbricated scales, which are ovate, obtuse, and keeled. A low prostrate shrub. Not introduced.

5. *T. brevifolia,* Nuttall. — Pacific Coast Yew. Western North America. Leaves falcate, short; midrib slightly prominent above; apex mucronate. Buds large, with loosely imbricated yellowish-green scales, which are lanceolate, mucronate, and keeled. A tree up to 50 feet high. Rare in cultivation.

6. *T. floridana,* Chapman. — Florida Yew. Western Florida. Leaves very narrow, midrib scarcely prominent, apex acute and mucronate. Buds small, with loosely imbricated ovate rounded obtuse keeled scales. A shrub or small tree. Not introduced.

7. *T. globosa,* Schlechtendal. — Mexican Yew. Leaves variable, narrow, straight, acuminate, mucronate. Buds with numerous ovate rounded obtuse keeled scales. A tree up to 25 feet high. Not introduced.

37.—*AUSTROTAXUS.*

A tree up to 75 feet high. *Leaves* spirally arranged, pectinate in two sets, spreading in one plane; linear or linear-lanceolate, up to 4 in. long, with recurved margins; upper surface flat or concave, with a deep median groove; lower surface with a prominent midrib and indistinct stomatic lines; apex acute. *Seed* ovoid or ellipsoidal, ½–¾ in. long, surrounded by a fleshy aril, open at the top.

Only one species, *A. spicata,* Compton, is known, a native of New Caledonia. It is not yet introduced, and its economic value is not known. Plate 15, fig. 68.

38.—*AMENTOTAXUS.*

A shrub up to 10 feet high. *Leaves* spirally arranged, pectinate, in two sets, spreading in one plane; linear to linear-lanceolate, up to 4 in. long and ¼ in. broad; acuminate, with a sharp-pointed apex; upper surface convex, with a prominent midrib; lower surface with a midrib and two glaucous white stomatic bands, margined by two broad green bands.

Only one species, *A. argotaenia,* Pilger, is known, occurring in Hongkong, Formosa, and West China. It is not yet introduced, and is of no economic value. Plate 15, fig. 67.

39.—*TORREYA.*

Usually medium-sized trees. *Branchlets* opposite or sub-opposite on the main axis of the branch. *Buds* with few decussate scales, all deciduous, or two to four persisting, minute, and inconspicuous, at the base of the branchlet. *Leaves* spirally arranged, pectinate in two sets, spreading in one plane; linear or linear-lanceolate; apex acuminate, tipped with a bristle-like cartilaginous point; upper surface convex; lower surface with a green midrib, and two white stomatic bands sunk in longitudinal depressions; fibro-vascular bundle undivided, with a solitary resin-canal beneath it. *Fruit* ellipsoid or obovoid, up to 1½ in. long, drupe-like, with an outer succulent resinous coat and an inner woody shell; ripening in the second year.

There are five living species, occurring in California, Florida, China, and Japan.

The genus is of small economic importance. The wood is of good quality, close-grained, pale yellow in colour, and durable. It is used locally for furniture making and other purposes.

1. *T. californica,* Torrey. — California. Leaves linear, 1¼–3 in. long, ⅛ in. broad; glaucous beneath, with a broad midrib and slightly depressed, narrow stomatic bands. Leaves and branchlets with a pungent aromatic odour when bruised. Up to 90 feet high. Cultivated for ornament.

2. *T. nucifera,* Siebold and Zuccarini. — Japan. Leaves lanceolate-linear, ¾–1¼ in. long, ⅛–⅙ in. broad; lower surface with a midrib and two deeply depressed broad stomatic bands. Plate 11, fig. 27. Leaves and branchlets with a pungent aromatic odour when bruised. Up to 80 feet high. Cultivated for ornament.

3. *T. grandis,* Fortune.—China. Leaves lanceolate-linear, ½–1 in. long, ⅛ in. broad; thinner in texture than those of *T. nucifera,* but with similar stomatic bands. Leaves and branchlets without a peculiar odour when bruised. Up to 80 feet high. Rare in cultivation.

4. *T. taxifolia,* Arnott.—Florida. Leaves linear, ¾–1½ in. long, ⅛ in. broad, pale green beneath, with a broad midrib, and narrow scarcely depressed stomatic bands. Leaves and branchlets with a disagreeable odour when bruised. Up to 40 feet high. Rare in cultivation.

40.—*CEPHALOTAXUS.*

Shrubs or small trees. *Buds* with numerous imbricated scales, which persist as a conspicuous sheath after the growth of the branchlet. *Leaves* spirally arranged, pectinate, in two sets, spreading in one plane or forming a V-shape; linear, up to 3 in. long, acute and sharp-pointed at the apex; upper surface with a prominent midrib sunk in a depression; lower surface with two white stomatic bands; fibro-vascular bundle undivided, with a single resin-canal beneath it. *Branchlets* opposite or sub-opposite on the main axis of the branch. *Fruit* ellipsoid or obovoid, up to 1¼ in. long, drupe-like, with a fleshy outer covering, and a hard woody inner shell.

Six species are known, living in China, Japan, Khasia Mountains, Assam, and Munnipore.

The wood is too small to be of economic importance.

1. *C. drupacea,* Siebold and Zuccarini. Japan and Central China. Leaves usually in a V-shaped arrangement, ¾–1½ in. long, straight or curved, tapering towards the acute usually spine-tipped apex; lower surface with two stomatic bands, each of 13–15 lines. A bushy tree up to 25 feet high. Cultivated for ornament.

2. *C. Fortunei,* W. J. Hooker.—China. Leaves in two ranks, spreading in one plane, 1½–3 in. long, curved, tapering to an acuminate, usually spine-tipped apex; lower surface with conspicuously white stomatic bands, each of 18–21 lines, covering nearly the whole surface. A tree up to 40 feet high. Cultivated for ornament.

3. *C. pedunculata,* Siebold and Zuccarini. — Japan. Leaves in two ranks, spreading either in one plane or in a V-shaped arrangement, straight or curved, 1½–2 in. long, tapering to an acute often spine-tipped apex; lower surface with broad stomatic bands, each of 16–21 lines. Plate 11, fig. 28. A large shrub or a small tree. Cultivated for ornament.

3A. *C. pedunculata,* var. *fastigiata,* Carrière.—A fastigiate form similar to the Irish Yew in habit; branches and branchlets directed vertically upwards; leaves spreading radially on the branchlets. A shrub. Cultivated for ornament.

The following species have not been introduced:—

4. *C. Griffithii,* Hooker.—Assam.
5. *C. Mannii,* Hooker.—India.
6. *C. Oliveri,* Masters.—China.

41.—*PHEROSPHAERA.*

Low growing shrubs. *Leaves* spirally arranged, differing in the two species. *Cones* ovoid, about $\frac{1}{10}$ in. long, with 4–8 thin scales. Seeds, several in each cone.

Two species are known, natives of New South Wales and Tasmania. They are not yet introduced, and are of no economic importance.

1. *P. Fitzgeraldii,* F. V. Mueller.—New South Wales. Leaves $\frac{1}{8}$ in. long, curved, decurrent, broad at the base, gradually narrowing towards the apex; trigonous; ventral surface with a stomatic band; dorsal surface keeled. Ultimate branchlets very slender. Plate 10, fig. 21.

2. *P. Hookeriana,* Archer.—Tasmania. Leaves scale-like, closely appressed, rhombic-ovate, convex on the back, with a rounded apex. Ultimate branchlets terete, $\frac{1}{16}$ in. in diameter. Plate 10, fig. 13.

42.—*DACRYDIUM.*

Trees or shrubs. *Leaves* spirally arranged; in most species scale-like, closely appressed, rhombic-ovate, convex or angular on the back, with distinct scattered stomatic lines; in a few species linear and wide-spreading. *Seed* solitary, ovoid, up to $\frac{1}{8}$ in. long, with a membranous shell, surrounded at the base by a cup or disc.

About eighteen species have been described, living in New Zealand, Tasmania, New Caledonia, Philippines, Malay Peninsula and Archipelago, Borneo and Chile.

Two species are important timber trees in their native country. The wood is yellow to light red in colour, very durable and strong. It is used for building construction, railway sleepers, furniture making, and the indoor finish of houses.

I.—LEAVES SCALE-LIKE, APPRESSED.

1. *D. Franklini,* J. D. Hooker.—Huon Pine. Tasmania. Leaves sharply angular on the back, with an acute incurved apex. Ultimate branchlets terete, $\frac{1}{30}$ in. in diameter. An important forest tree in its native country, where it attains a height of 100 feet. Cultivated for ornament.

2. *D. Bidwillii,* J. D. Hooker. — Mountain Pine. New Zealand. Leaves angular on the back, with an obtuse apex. Ultimate branchlets terete, $\frac{1}{25}$ in. in diameter. A shrub up to 10 feet high. Rare in cultivation.

3. *D. biforme,* Pilger.—New Zealand. Leaves angular on the back, with an acute apex. Ultimate branchlets terete, $\frac{1}{12}$ in. in diameter. A tree up to 40 feet high. Not introduced. Plate 10, fig. 10.

4. *D. laxifolium,* J. D. Hooker.—New Zealand. Leaves convex on the back, with a rounded apex, closely appressed on the ultimate branchlets, but spreading on the main axes of the branch. Ultimate branchlets terete, $\frac{1}{16}$ in. in diameter. A prostrate shrub. Not introduced.

II.—LEAVES LINEAR, SPREADING.

5. *D. cupressinum,* Solander.—New Zealand. Leaves up to $\frac{1}{3}$ in. long, curved, decurrent and broad at the base, gradually narrowing towards the apex, tetragonal. A tree up to 100 feet high in its native country, where it is an important forest tree. Rare in cultivation.

43.—*ACMOPYLE.*

A tree up to 50 feet high. *Leaves* spirally arranged on lateral branchlets, pectinate, spreading in two sets in one plane, up to $\frac{1}{2}$ in. long, curved, decurrent and broad at the base, gradually narrowing towards the apex; flattened, oval in cross-section; resin-canal solitary, eccentric and lateral; upper surface with indistinct stomatic lines; lower surface with two broad glaucous stomatic bands. *Fruit* drupe-like, with a large fleshy receptacle, bearing a single seed.

Only one species, *A. Pancheri,* Pilger, is known, a native of New Caledonia. It has been introduced, but is rare in cultivation. Plate 10, fig. 22, and Plate 15, fig. 70.

The economic value of Acmopyle is not known.

44.—*PODOCARPUS.*

Trees or shrubs. *Leaves* spirally arranged, very variable in size and shape: (*a*) minute and scale-like, (*b*) linear, or (*c*) large ovate or lanceolate. *Seed* ovoid or globose, up to 1 in. long, drupe-like, with a dry or fleshy outer integument, and a woody inner shell, borne on a dry or fleshy receptacle.

About seventy-five species are known, of which fourteen have been introduced, and are in cultivation as ornamental trees. The genus is widely spread throughout the warm, temperate, and sub-tropical regions of the Southern Hemisphere, occurring in Japan, China, India, Malay States, New Zealand, Africa, South America, and Philippine Islands.

Many species are important timber trees in their native countries. The wood is straight-grained, hard, durable. It is used for building construction, sleepers, furniture, and many other purposes.

The genus is divided into five sections:

I.—Nageia, Endlicher.

Leaves opposite or sub-opposite, ovate or ovate-lanceolate, with many parallel veins, underneath which the resin-canals are situated. Seed axillary; receptacle fleshy or dry.

Eight species, including *P. Nagi,* Zollinger; *P. Wallichianus,* C. Presl.

II.—Eupodocarpus, Endlicher.

Leaves opposite, sub-opposite, alternate, or whorled, linear to narrowly lanceolate, with a central vein. Seeds borne on a fleshy receptacle.

Thirty-eight species, including *P. neriifolius,* D. Don; *P. Totara,* A. Cunningham; *P. macrophyllus,* D. Don; *P. Hallii,* Kirk; *P. latifolius,* R. Brown; *P. nivalis,* J. D. Hooker; *P. Purdieanus,* Hooker; *P. elongatus,* L'Héritier; *P. chilinus,* Richard; *P. nubigenus,* Lindley; *P. Henkelii,* Stapf; *P. alpinus,* R. Brown; *P. milanjianus,* Rendle.

III.—Stachycarpus, Endlicher.

Leaves opposite, sub-opposite, alternate, or whorled, linear to narrowly lanceolate, with a central vein. Seed without a fleshy receptacle.

Fourteen species, including *P. montanus,* Loddiges; *P. ferrugineus,* D. Don; *P. spicatus,* R. Brown; *P. andinus,* Pilger; *P. falcatus,* R. Brown; *P. gracilior,* Pilger.

IV.—Dacrycarpus, Endlicher.

Leaves scale-like. Seed solitary, terminal on a fleshy receptacle.

Four species, including *P. dacrydioides,* A. Richard; *P. imbricatus,* Blume.

V.—Microcarpus, Pilger.

Leaves scale-like. Seed solitary, terminal on a short pendulous branchlet; receptacle not fleshy. One species.

P. ustus, Brongniart and Gris.

A.—LEAVES OVATE OR OVATE-LANCEOLATE, WITHOUT A MIDRIB ON EITHER SURFACE.

1. *P. Wallichianus,* C. Presl.—Khasia, Assam, Burma. Leaves up to 7 in. long, with a long acuminate point. A tree. Not introduced.

2. *P. Nagi,* Zollinger.—Japan and Formosa. Leaves up to 3 in. long, with a short acuminate point. Plate 12, fig. 36. A tree up to 80 feet high. Grown indoors at Kew.

B.—LEAVES LANCEOLATE, WITH A PROMINENT MIDRIB ON BOTH SURFACES.

3. *P. neriifolius,* D. Don.—Himalayas, China, Philippines, Malay Archipelago. Leaves up to 7 in. long and ½ in. wide; upper surface dark green; lower surface not glaucous. An important timber tree up to 60 feet high. Rare in cultivation.

4. *P. macrophyllus,* D. Don.—China and Japan. Leaves up to 5 in. long and ½ in. wide; upper surface bright green; lower surface glaucous. Plate 12, fig. 37. A tree up to 50 feet high. Rare in cultivation.

5. *P. latifolius,* R. Brown.—South Africa. Leaves up to 3 in. long and ⅓ in. wide. An important timber tree up to 70 feet high. Not introduced.

6. *P. Purdieanus,* Hooker.—Jamaica. Leaves up to 4 in. long and ⅔ in. wide. A tree up to 120 feet high. Not introduced.

C.—LEAVES NARROWLY LANCEOLATE, MORE THAN THREE INCHES LONG, MIDRIB PROMINENT ON BOTH SURFACES.

7. *P. chilinus,* Richard.—Chile. Leaves up to 5 in. long and ¼ in. wide, invariably falcate. An important timber tree up to 70 feet high. In cultivation.

8. *P. Henkelii,* Stapf.—South Africa. Leaves up to 6 in. long and ⅓ in. wide, straight or falcate. An important timber tree. Not introduced.

D.—LEAVES LINEAR, LESS THAN THREE INCHES LONG.

(I). Leaves without visible stomatic lines.

(a) Leaves without a prominent midrib on the upper surface.

9. *P. Totara,* A. Cunningham.—New Zealand. Leaves up to 1 in. long, with a median groove in the upper surface. Plate 11, fig. 30. An important timber tree up to 100 feet high. In cultivation.

10. *P. nivalis,* J. D. Hooker.—New Zealand. Leaves up to ¾ in. long, with the upper surface concave. A shrub up to 6 feet high. In cultivation.

(b) Leaves with a prominent midrib on the upper surface.

11. *P. elongatus,* L'Héritier.—Western South Africa. Leaves up to 2 in. long. An important timber tree up to 70 feet high. In cultivation.

(II). Leaves with indistinct stomatic lines on the lower surface.

12. *P. Hallii,* Kirk.—New Zealand. Leaves alternate, irregularly spreading, up to 1½ in. long, with a median groove on the upper surface. An important timber tree up to 60 feet high. In cultivation.

13. *P. montanus,* Loddiges. — Peru, Colombia, Costa Rica, Venezuela, and Bolivia. Leaves opposite, pectinate, spreading in one plane, with a midrib on the upper surface. An important timber tree up to 60 feet high. Rare in cultivation.

(III). Leaves with conspicuous stomatic bands on the lower surface.

14. *P. nubigenus,* Lindley.—Chile and Patagonia. Leaves up to 1¾ in. long, rigid, acuminate, with a sharp cartilaginous point; upper surface with a prominent midrib. Plate 11, fig. 26. A large tree. In cultivation.

15. *P. andinus,* Pilger (*Prumnopitys elegans,* Philippi).—Chile and Patagonia. Leaves up to 1 in. long, soft, acute at the apex, with a sharp horny point; upper

surface with an inconspicuous midrib. Plate 11, fig. 24. A tree up to 40 feet high. In cultivation.

E.—LEAVES SCALE-LIKE.

16. *P. dacrydioides,* A. Richard.—New Zealand. Leaves $\frac{1}{16}$ in. long, keeled on the back, sometimes with indistinct stomatic lines, and tapering towards the incurved mucronate apex. Plate 10, fig. 11. An important timber tree up to 150 feet high. Rare in cultivation.

45.—*SAXGOTHAEA.*

A shrub or tree up to 40 feet high. *Leaves* spirally arranged, pectinate, in one plane, usually twisted or curved, $\frac{1}{2}$–$\frac{3}{4}$ in. long, linear; upper surface with a prominent midrib; lower surface with two conspicuous stomatic bands; apex acute, mucronate; central resin-canal. *Fruit* globose, $\frac{1}{2}$ in., with fleshy scales.

Only one species, *S. conspicua,* Lindley, is known, occurring in Chile and West Patagonia; and rare in cultivation. Plate 11, fig. 25.

The wood is too small to be of much economic value, and is used locally.

46.—*MICROCACHRYS.*

A low straggling shrub. *Leaves* in opposite decussate pairs, scale-like, ovate, convex on the back, closely appressed and densely imbricate; apex rounded, incurved. Ultimate branchlets tetragonal, equal-sided, $\frac{1}{25}$ in. wide; some long and whip-like. *Fruit* ovoid or globular, $\frac{1}{3}$ in. long. Seeds, one on each fertile scale, surrounded by a red fleshy aril.

Only one species, *M. tetragona,* J. D. Hooker, is known, occurring in Tasmania, and of no economic value. It is introduced, but is rare in cultivation. Plate 14, fig. 49.

47.—*PHYLLOCLADUS.*

Trees or shrubs. *Leaves* and *cladodes* spirally arranged. Cladodes (*i.e.,* modified branchlets resembling true leaves) flat, rhomboidal, arising each out of the axil of a scale-like leaf. *Seed* ovoid, $\frac{1}{4}$ in. long, enclosed at the base in a cup-shaped disc; solitary, or several together in a globular cone-like structure.

Six species have been described, occurring in Tasmania, New Zealand, Philippine Islands, New Guinea, and Borneo.

The species described below produce commercial timber in their native countries. The wood is straight-grained, heavy, and hard. It is used for building construction, sleepers, pit-props, and for furniture and indoor work. Several species have been introduced, but are rare in cultivation.

1. *P. rhomboidalis,* Richard.—Tasmania. Cladodes fan-shaped or rhomboidal, obtuse; serrate, lobed, and not crenate in margin, 1–2 in. long. Plate 13, fig. 38.

Seeds usually 3–4 together in cones, ¼ in. long and wide. A tree up to 60 feet high.

2. *P. trichomanoides,* D. Don. — New Zealand. Cladodes fan-shaped or broadly ovate, lobed, serrate and crenate in margin, ¼–1 in. long and wide. Seed solitary, enclosed at the base in a thin membrane, surrounded by a swollen cup, formed by the fusion of the two fleshy scales. A tree up to 60 feet high.

3. *P. glaucus,* Carrière. — New Zealand. Cladodes pinnate, 5–12 in. long, with 9–17 lobes, fan-shaped or rhomboidal, serrate and not crenate in margin, up to 2 in. long and 1¼ wide, usually glaucous. Seeds, 10–20 together in cones about ½ in. long and ⅓ in. wide. A tree up to 40 feet high.

The following species are small trees, of no economic importance:—

4. *P. alpinus,* J. D. Hooker.—New Zealand.

5. *P. hypophyllus,* J. D. Hooker. — Philippine Islands, New Guinea, and Borneo.

6. *P. major,* Pilger.—New Guinea.

EXPLANATION OF PLATES.

The figures are natural size, except where otherwise stated.

Plate 9.

Fig.
1. *Abies grandis.*
2. *Keteleeria Davidiana.*
3. *Pseudotsuga Douglasii.*
4. *Picea spinulosa.*
5. *Tsuga Albertiana.*

Fig.
6A. *Pinus sylvestris.*
6B. *Pinus cembroides.*
6C. *Pinus Cembra.*
7. *Larix europaea.*
8. *Pseudolarix amabilis.*

Plate 10.

9. *Cedrus Libani.*
10. *Dacrydium biforme.*
11. *Podocarpus dacrydioides.*
12. *Athrotaxis cupressoides.*
13. *Pherosphaera Hookeriana.*
14. *Cryptomeria japonica.*
15. *Taiwania cryptomerioides.* Juvenile foliage.
16. *Taiwania cryptomerioides.* Adult foliage.
17. *Wellingtonia gigantea.*
18. *Araucaria Cunninghamii.*
19. *Athrotaxis selaginoides.*
20. *Athrotaxis laxifolia.*
21. *Pherosphaera Fitzgeraldii.*
22. *Acmopyle Pancheri.*
23. *Sequoia sempervirens.*

PLATE 11.

Fig.
24. *Podocarpus andinus.*
25. *Saxegothaea conspicua.*
26. *Podocarpus nubigenus.*
27. *Torreya nucifera.*
28. *Cephalotaxus pedunculata.*
29. *Taxus baccata.*
30. *Podocarpus Totara.*
31. *Glyptostrobus pensilis.*
32. *Taxodium distichum.*

PLATE 12.

33. *Cunninghamia sinensis.*
34. *Araucaria Bidwillii.*
35. *Agathis australis.*
36. *Podocarpus Nagi.*
37. *Podocarpus macrophyllus.*

PLATE 13.

38. *Phyllocladus rhomboidalis.*
39. *Sciadopitys verticillata.*
40. *Cupressus Lawsoniana.*
41. *Thuya plicata.*
42. *Biota orientalis.*
43. *Microbiota decussata.*
44. *Thujopsis dolabrata.*
45. *Libocedrus decurrens.*
46. *Fokienia Hodginsii.*
A. Adult foliage.
B. Juvenile foliage.
47. *Cupressus macrocarpa.* (Slightly mag.)
48. *Widdringtonia Schwarzii.*

PLATE 14.

49. *Microcachrys tetragona.*
50. *Diselma Archeri.*
51. *Juniperus chinensis.*
A. Scale-like foliage.
B. Acicular foliage.
52. *Libocedrus tetragona.*
53. *Fitzroya patagonica.*
54. *Juniperus communis.*
55. *Callitris oblonga.*
56A. *Actinostrobus pyramidalis.*
56B. *Actinostrobus acuminatus.*
57. *Tetraclinis articulata.*
58. *Callitropsis araucarioides.*
59. *Araucaria Cookii.*
60. *Cupressus sempervirens.*
61. *Cupressus torulosa.*
62. *Cupressus cashmeriana.*
63. *Cupressus nootkatensis.*
64. *Juniperus drupacea.*
65. *Juniperus recurva.*
66. *Juniperus virginiana.*

PLATE 15.

67. *Amentotaxus argotaenia.*
68. *Austrotaxus spicata.*
69A. Cross-section through leaf of *Abies grandis,* showing marginal resin-canals. × 40.
69B. Cross-section through leaf of *Abies balsamea,* showing median resin-canals. × 40.
70. Cross-section through leaf of *Acmopyle Pancheri,* showing eccentric resin-canal B. beside vascular-bundle A. × 40.
71A. Cross-section through leaf of *Pinus echinata,* showing median resin-canals. × 20.
71B. Cross-section through leaf of *Pinus Laricio,* showing median resin-canals. × 20.
71C. Cross-section through leaf of *Pinus sinensis,* showing marginal resin-canals. × 20.
72A. Cross-section through leaf of *Pseudotsuga Douglasii.* × 20.
72B. Cross-section through leaf of *Pseudotsuga glauca.* × 20.
73. Bud of *Pinus sinensis.*
74. Bud of *Pinus montana.*
75. Bud of *Pinus contorta.*
76. Bud of *Pinus Laricio.*

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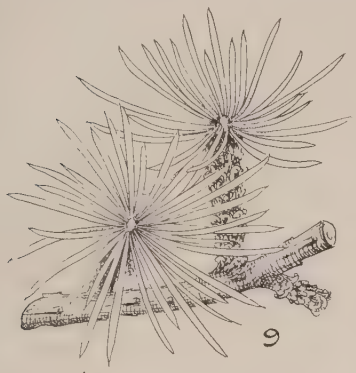
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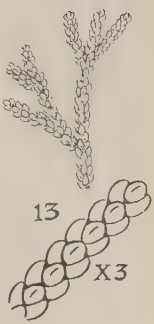
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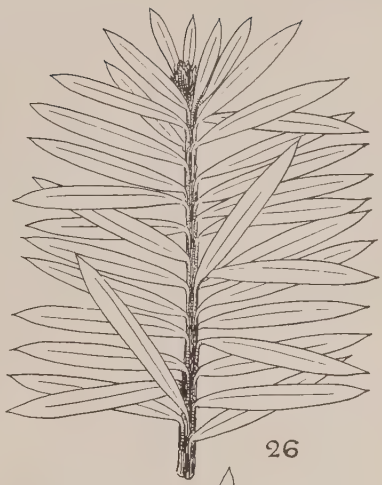
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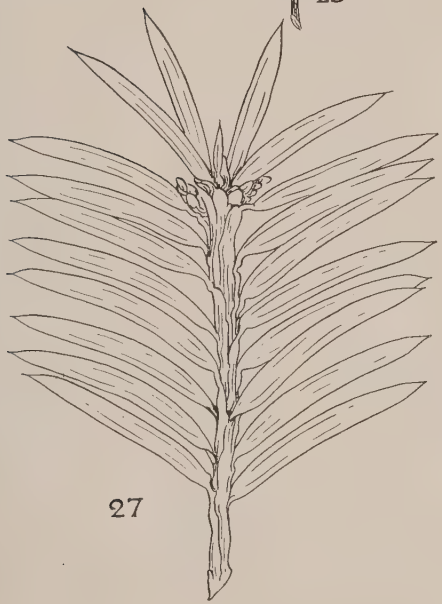
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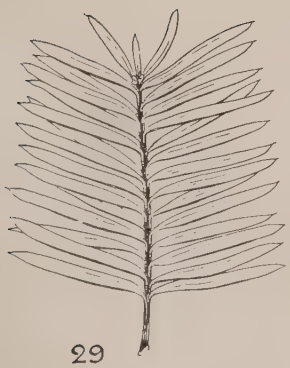
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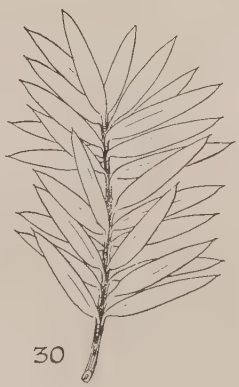
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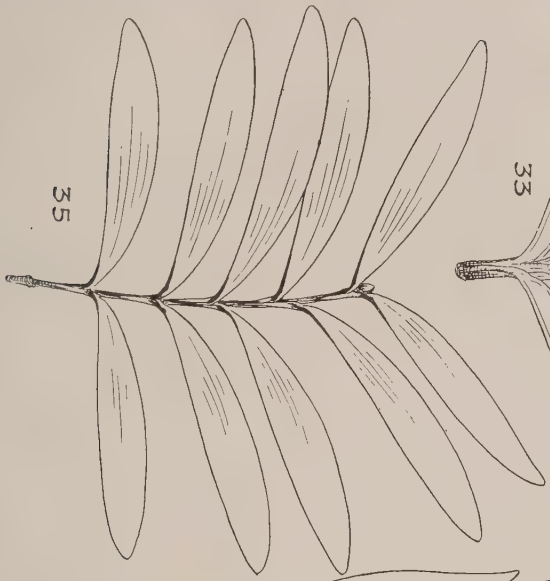
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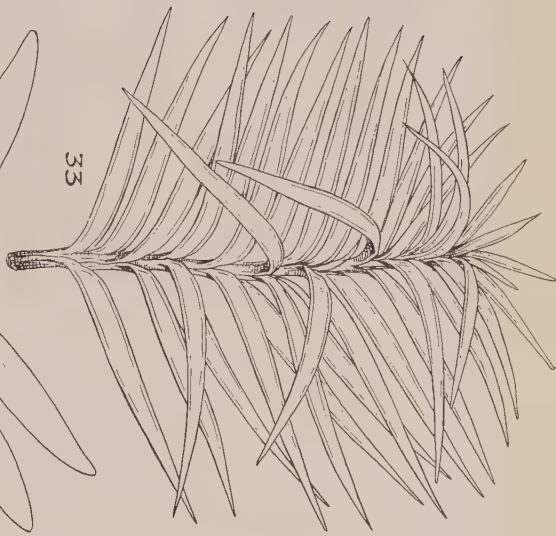
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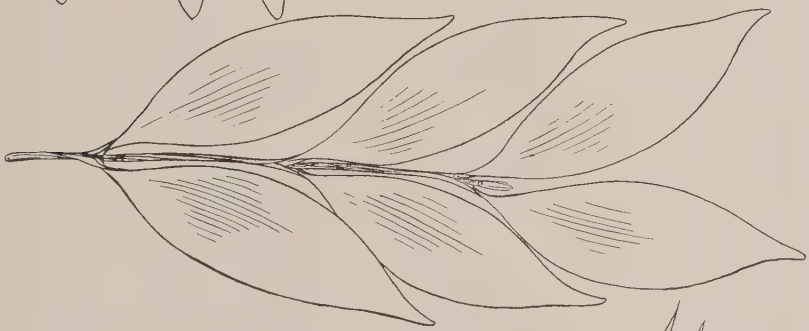
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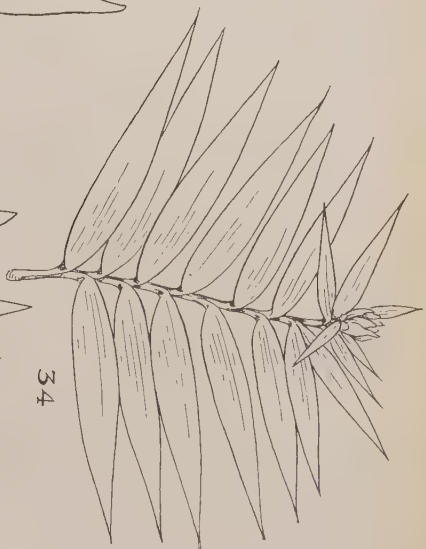
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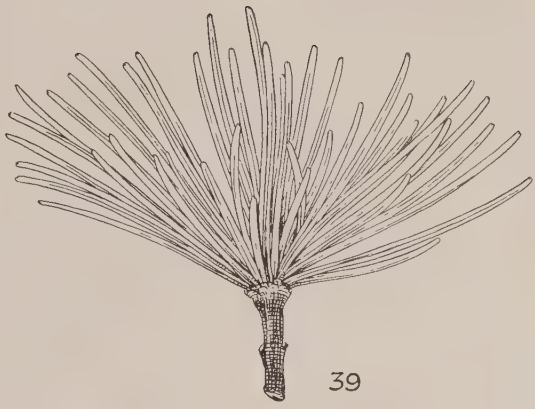
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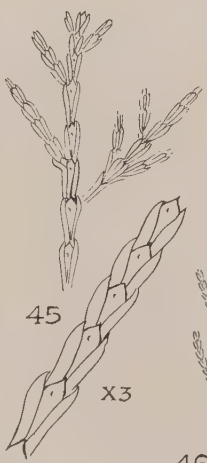
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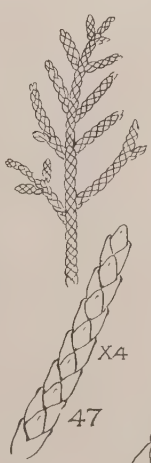
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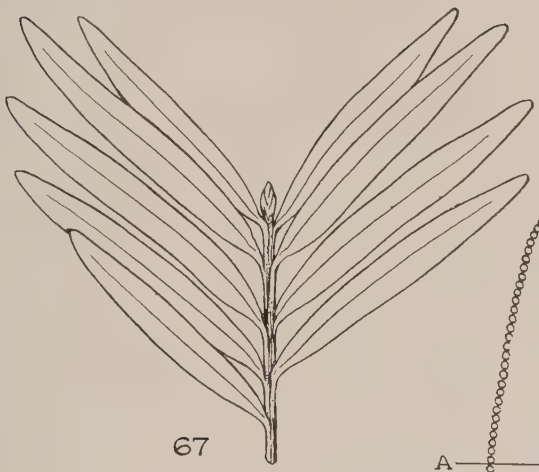
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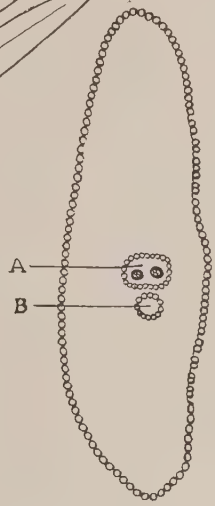

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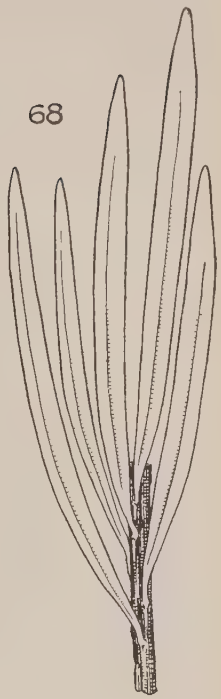
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No. 20.

A STUDY OF LACTOSE-FERMENTING YEASTS ISOLATED FROM MILK, CREAM, AND BUTTER.

By M. GRIMES and J. DOHERTY,
Dairy Science Department, University College, Cork.

[Read March 26. Published separately May 6, 1929.]

Lactose-fermenting yeasts are of importance in the dairy industry owing to their producing undesirable changes in dairy products, and also as a factor in interfering with the normal churning of cream, when cream is held for several days before churning, as is done in home butter-making. They have the ability to grow under conditions that are unfavourable for the growth of most bacteria, and may grow in the presence of large amounts of acid. Several of the original cultures of the lactose-fermenting yeasts dealt with in this paper were isolated from milk and cream having an acidity of 0·80 to 1·50 per cent. lactic acid.

In two cases they were found present in samples of milk, contained in sealed bottles that were six weeks old. When the stoppers were removed the contents frothed up and poured over the rims of the bottles. In two cases they were isolated from samples of gassy cream. The cream had been held from three to five days before churning, and the cream failed to churn owing to frothing in the churn.

Lactose-fermenting yeasts are known to be widely distributed. There is a considerable amount of literature concerning them which gives more or less recognisable descriptions of the cultures isolated. It is not intended to review the literature, as this has been done by Hammer (1) and Harrison (2), (3). In their general grouping of yeasts found in dairy products, Cordes and Hammer (4) include under Group III—

Yeasts showing white, smooth-edged colonies and pronounced gas formation in milk.

a. Optimum near 37° C.; cells oval. *Torula cremoris.*

2a. Growth slow, if at all, at 37° C.; but good at 30° C.; cells spherical. *Torula sphaerica.*

In the course of the routine examination of milk, cream, and butter in this laboratory, it has been customary to estimate the number of yeasts and moulds per c.c. The samples of milk, cream, etc., were examined for yeasts and moulds

by plating on lactose agar, 0·5 c.c. of a 4 per cent. solution of lactic acid being added to each plate just before pouring, and incubating at 20° C. for a week.

The yeasts were generally white, smooth-edged colonies, with the exception of those producing pink colonies. In all cases the cells were oval. From time to time these yeast colonies were inoculated into litmus milk, and in that way eleven lactose-fermenting yeasts were isolated from milk, cream, and butter. These yeasts caused gas formation and produced slight acidity in milk. They were systematically examined, and were found to consist of two types referred to as Type A and Type B.

Type A, eight cultures were isolated from milk (5), cream (2), and butter (1).

Type B, three cultures were isolated from milk.

The preparation of the media used for classification is not given, as standard methods were used. The yeasts differed mainly in size and fermentation reactions.

Type A.—Cells oval or elliptical. When grown at 37° C. the tendency was for the cells to be stouter than when grown at 20° C., and, in some cases, to be nearly spherical, average size 3·0μ.

When grown on lactose agar slants at 20° C., the cells varied from 2·0μ to 4·0μ in length, and from about 1·5 to 3·0μ in width.

Spore formation was not observed, and the organism is considered to be a Torula. The cells stained readily with the ordinary stains, and were gram positive in young cultures. In old cultures gram negative cells were sometimes observed.

Type B.—Cells oval or elliptical. More definitely oval when grown at 37° C. than Type A.

When grown on lactose agar slants the cells were from 4 to 6μ long and about 2 to 3μ wide.

Spore formation was not observed, and the organism is considered to be a Torula.

The cells stained readily with the ordinary stains and were gram positive in young cultures.

Cultural Characters.

Lactose agar plate.—Colonies visible in 48 hours at 37° C. When 96 hours old, surface colonies averaged 2 to 4μ in diameter, circular, whitish, glistening, smooth, raised, opaque, with an entire edge; some may grow larger up to 7μ. Sub-surface colonies were generally oval in shape and had an entire edge. When plates were opened there was a pleasant fruity odour.

Nutrient agar plate.—Growth slower than on lactose agar, but possessed the same general characteristics.

Lactose agar slant.—After 48 hours at 37° C. growth good, white, glistening, opaque, smooth, raised, edge entire or slightly undulate.

Nutrient agar slant.—Growth slower than on lactose agar, but possessed the same general characteristics.

Nutrient gelatine stab.—In 4 to 6 days good surface growth, whitish, smooth, raised, glistening. Along the line of stab the growth was filiform and heaviest near the surface.

Nutrient broth.—Growth was evident in from 48 to 72 hours by cloudiness and a whitish sediment.

Dunham's Solution. — Good growth evidenced by cloudiness and whitish sediment in bottom of test-tube.

Litmus milk.—After 24 to 48 hours at 37° C. definite gas evolution, more marked on shaking test-tube, slight acidity developed. There was slight coagulation often after holding at 37° C. for two weeks or longer. No coagulation in three weeks at 20° C. Counts at four to seven days from 10 to 25 million per c.c.

Potato slope at 20° C. — Good growth in from 48 to 72 hours. Growth slightly raised, whitish, glistening, smooth, opaque, definite edge.

Gas Production.

Type A.—Acid and gas were produced in milk and cream, and in bouillons containing glucose, lactose, saccharose. No gas was produced in bouillons containing glycerol, inulin, maltose, mannitol, salicin. Of the eight cultures one produced gas in galactose and one produced gas in levulose. The other cultures did not produce gas in galactose nor levulose bouillons. The differentiation among these cultures in their ability to ferment galactose and levulose is not considered sufficient to differentiate them, as it is known that in the case of galactose adaptation occurs (5).

Type B.—Acid and gas were produced in milk and cream and in bouillons containing galactose, glucose, lactose, levulose, and saccharose. Of the three cultures, two produced gas in inulin bouillon, whilst one was negative. No gas was produced in bouillons containing glycerol, maltose, mannitol, salicin.

Optimum Temperature.

When the cultures were first isolated they grew better at 20° C. than at 37° C., but finally best growth was obtained at 37° C. in all cases, with the exception of two cultures included in Type A which all the time grew best at 20° C. This suggests that there is a wide range of temperature to which yeasts can adapt themselves to give good growth.

A study of the recognised descriptions in the literature showed that the cultures included under Type A were similar to, or identical with, *Torula lactosa*, Harrison (2), isolated from Canadian cheese; and that the cultures included under Type B are similar to, or identical with, *Torula cremoris*, Hammer, isolated from yeasty cream.

Acknowledgment is made to the Curator, The National Collection of Type Cultures for cultures of *Torula cremoris* and *Torula sphaerica* sent for purposes of comparison.

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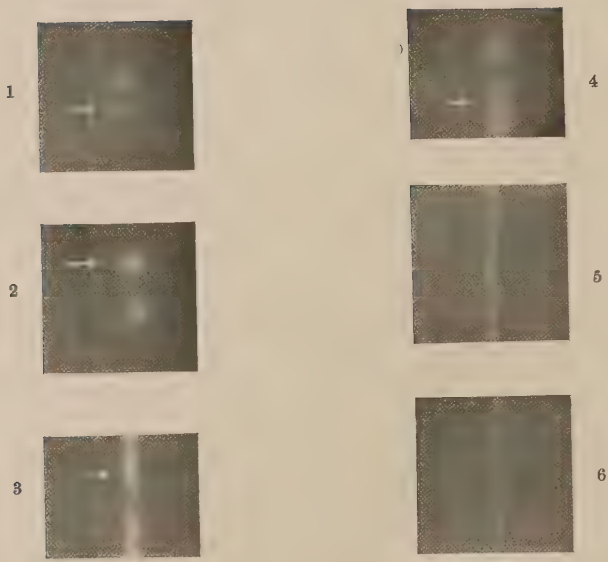
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No. 21.

THE EFFECT OF STRONG MAGNETIC AND ELECTRIC FIELDS ON THE RECTILINEAR PROPAGATION OF γ RAYS.

By J. H. J. POOLE, Sc.D.,

AND

A. G. CLARKE, B.A.

(Plate 16.)

[Read March 26. Published separately May 22, 1929.]

It has been held for many years, and probably correctly, that neither magnetic nor electric fields are capable of deflecting a γ ray beam. As now, however, it is being found that an electron possesses properties which we can only explain on the hypothesis that it can act, in some cases, as a wave group of very high frequency, it is perhaps not unreasonable to imagine that γ rays of about the same frequency might show certain properties akin to those of a charged particle. Sir J. J. Thomson has discussed this problem in a paper in the *Philosophical Magazine* for December, 1928. He has shown that we might conceive that γ rays, exceeding a certain frequency, would be deflected in passing through a dielectric in which a large transverse electric field was maintained. The γ rays from *RaC* are of sufficiently short wave-length to show the anticipated effect. Sir J. J. Thomson has conducted some experiments on these lines, and, in all cases except one, no effect due to the electric field could be detected. In the first trial, however, using mica as a dielectric, an apparently positive result was obtained. It was found impossible to repeat this experiment, and Sir J. J. Thomson accordingly seems inclined to attribute this solitary positive result to some spurious effect, perhaps due to scattered β ray radiation.

However, as this one unexplained positive result had been obtained with an electric field, it was thought worth while to see if any similar effect could be observed with a transverse magnetic field. Fortunately a small Weiss Magnet, capable of giving quite large fields, was available, and this enabled us to conduct the required trials with comparative ease.

Fig. 1 shows the arrangement adopted. The γ rays are obtained from a short emanation tube placed perpendicular to the plane of the diagram and parallel to the lead slit system. This slit system is made out of two rectangular lead blocks, about 1·5 cm. deep by 2 cm. wide by 8 cm. long. These blocks were kept apart by two narrow distance-pieces along either side, so that, by varying the thickness of these pieces, a slit of any desired width could be

obtained. To hold the lead blocks and the distance-pieces together, four small-diameter bolts passing through both blocks and distance-pieces were used. The emanation-tube end of the slit was slightly recessed, so that the tube could be easily fixed in position with a little plasticine or some convenient adhesive wax. The concentration of radon in the tubes when new varied from about 1 to 4 millicurie per millimetre length of tube. The external diameter was about 0·8 mm. and the internal diameter probably about 0·5 mm.

After passing through the slit, the γ rays then pass through the narrow air space between the circular pole-pieces of the electro-magnet. The distance between the two poles was generally about 2 mm., so that over a length of path of 8 cm. the γ ray beam was subjected to a fairly strong transverse magnetic field. The measurement of this field is described later. It is better to be content with the value of the field obtained with large-diameter flat pole-pieces, rather than to increase it by using conical ones, since, if we adopt this course, the gain due

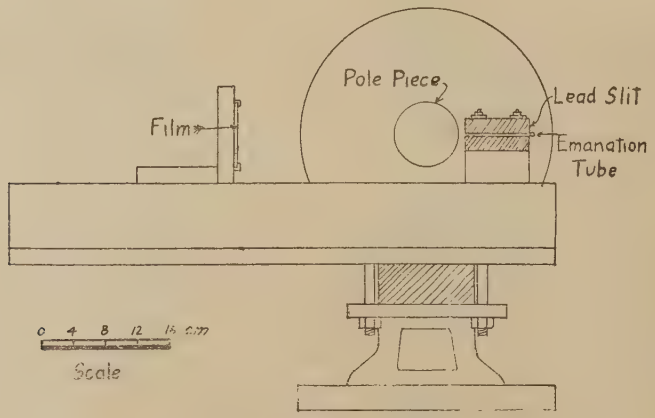

Fig. 1.

to the increased field will be outweighed by the loss produced by the shortening of the path in the field. If the γ ray acted in any way similarly to a charged particle, it would, of course, be deflected either upwards or downwards by this transverse field.

To detect whether this is the case or not, the γ ray beam, after traversing the magnetic field, falls on a dental X ray film, placed, as shown in sketch, some distance back from the magnet. Dental X ray films are very convenient for this purpose, as they are supplied in light-tight envelopes, and, if the type containing a double film is used, we obtain a double record of each experiment. This is useful if we are doubtful whether any mark on the film, when developed, may be due to a flaw in the film, or to some extraneous effect produced during development. It is, of course, highly improbable that both films would, in these cases, show the same effect. In these experiments this is an undoubted

advantage, as, owing to the long exposures entailed, and the consequent large consumption of emanation tubes, we cannot afford any avoidable repetition of our results.

The method adopted to show whether the γ ray beam was deflected by the field or not was as follows. A film was first exposed to the rays with the field on for a certain time, and then off for about an equal time. A second film was next exposed for a time equivalent to the first total exposure, but with the field off the whole time. If the field produces any deflection, the image obtained on the first film should be wider in a vertical direction than that on the second. This method is very simple, but it depends for its success on the rigidity of the system, as, if any alteration in the position of either slit or film is produced by turning the field on or off, we will get a spurious effect shown on the film.

To avoid this possibility, the connection between the slit and the film-holder was made very rigid, as shown in the sketch. It consisted of a rectangular wooden beam, 10 cm. deep by 5 cm. wide. This beam was clamped to the top of the magnet yoke by means of two $\frac{3}{8}''$ bolts and a wooden bridge piece, as depicted. This made a satisfactory arrangement, and enabled the beam to be rigidly held. The slit system was bolted down to a wooden block, which, in its turn, was screwed to the beam, while the film was held by a metal clip to a wooden support, which could be screwed down at any desired distance along the beam. As a matter of fact, the film-carrier was always kept at the same distance of about 20 cm. from the near end of the lead slit, as it was found that the divergence of the γ ray beam was rather large, as might be expected. The arrangement was not interfered with between two consecutive exposures except to insert a new film. As this was a very simple operation, no risk of disturbance was involved.

The field in the air gap was measured with a Grassot fluxmeter and a specially constructed thin search coil. It ranged from about 17,800 gauss for an exciting current of 10 amp. to 18,800 gauss for 14 amp. Larger currents than this overheated the magnet winding when used over long periods. Generally the exciting current was kept at about 12 amp., which gave a field of 18,400.

The results of some of the experiments are shown in the annexed plate. Photos 1 and 2 were obtained with a slit about 1 mm. wide, a distance between the pole-pieces of 2·25 mm., and a field in the gap of about 18,000 gauss. The film was placed in all trials at a distance of 20 cm. from the nearest end of the lead slit. For ease of comparison the film obtained with the field on and off has been printed on the same positive as that obtained with no field. The image given by the γ rays in the former case is marked on the photos with an arrow. The direction of the field is perpendicular to the arrow shaft, so that if the field had any effect we would expect the image to be wider horizontally with the field on and off than with no field. A casual inspection of the two first photos shows that there is certainly no very marked difference.

In fact, in the upper photo the marked image seems rather narrower, while in the second it is rather wider. It was felt that this appearance was due to the difference in strengths of the two negatives. Owing to the shortness of the gap between the pole-pieces, it was difficult to obtain reasonably strong images, even with exposures of about three days. With these exposures the problem of keeping the magnet on for long periods without overheating was also troublesome, and the consequence was that, in many cases, the period of exposure with the field on was rather less than that with the field off.

To meet these objections, it was decided that it would be better to use a longer air-gap, even at the expense of obtaining a rather weaker magnetic field. Photo No. 3 shows the result of using a gap of 5 mm. and a slit of 0·5 mm. width. The marked image was obtained with an exposure of 57 hours, during exactly half of which the magnet was excited. The field in the gap was about 15,000 gauss. The lower image is with the field off. To compensate for the decay of the emanation during the first exposure, the exposure was doubled in this case. The result seems to confirm the view that a transverse magnetic field of this strength has no effect on the rectilinear propagation of a γ ray. Several other trials, not reproduced, which we made also agree with this conclusion.

Photo No. 4 shows the effect of placing a piece of iron between the pole-pieces and passing the γ ray beam through it, first with the field on and off, and secondly with the field off all the time. To demagnetise the iron when the current was turned off, the specimen was gently hammered. Again, however, no definite effect was obtained; in fact, the result of all our trials was to show that the transverse magnetic field produced no deflection of the γ ray beam which our methods were sufficiently delicate to detect.

When the experiments with the magnetic field had yielded a null result, it was thought that perhaps it would be worth while to repeat some of Sir J. J. Thomson's trials with the electric field. Unfortunately, however, no suitable source of high direct current voltage was available, and it was, accordingly, necessary to use an alternating voltage. It would, it is true, have been possible to rectify this voltage with a suitable rectifying valve, but this appears to be really unnecessary. If a γ ray is deflected by a direct transverse electric field, a narrow beam of rays will be drawn out sideways into a broader beam when passed through an alternating transverse electric field. It is, accordingly, only necessary to measure the width of the beam with the electric field on and off to detect whether this is so or not.

Fig. 2 is a sketch of the apparatus used to test this. As before, the main object is to secure rigidity in the various parts. This was most readily obtained by using an optical bench as the support for the various components, as it enabled us to adjust the different parts easily, while ensuring that they would be firmly held when once set.

The same lead slit was employed to produce the γ ray beam, but the width of the slit was reduced to about 0·2 mm. This reduction is necessary, since

the thickness of the dielectric, through which the beam passes, has also to be kept fairly small, about 2 to 3 mm., in order to enable us to obtain high potential gradients across it. If the γ ray beam is not decidedly narrower than the width of the dielectric, however, the effect of a small bending of the rays in the dielectric might be lost. The reduction in the width of the slit tends to increase the exposure, but this increase is, to a certain extent, compensated for by the fact that we can use a longer slit than in the magnetic

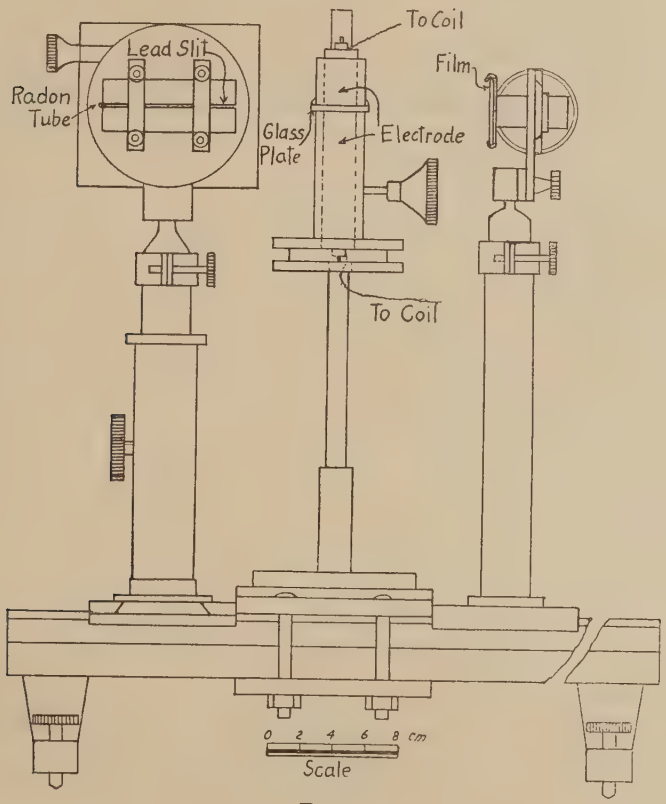

FIG. 2.

experiments, in which the narrow gap between the pole-pieces limited the available length. The slit system was mounted on one of the ordinary supporting pieces of the bench. This support enabled us to adjust the position of the slit in three dimensions, and also to rotate it about a vertical axis and a horizontal axis parallel to itself. The slit was firmly bolted to this support, so that no error could be introduced by any accidental motion during the course of an exposure.

The film-holder was fixed to the ordinary travelling eye-piece supplied with the bench. This eye-piece is carried by a pillar support, as shown, and by its use we can adjust the position of the film in three dimensions, and also rotate it about a vertical axis, if required. Between the lead slit and the film-holder a third support is placed to carry the dielectric material, together with the electrodes, for applying the alternating electric field. This support was not one of the ordinary bench ones, but was a special one, fitted with a rack and pinion motion, so that the height of the dielectric plate could be easily adjusted. The support was metal, but, to avoid possible danger from electric shocks to the observer, it was screwed to an ebonite base, which, in its turn, was fixed to a wooden cross-piece. This cross-piece was clamped to the bench with four bolts, which passed through a second wooden cross-piece, placed underneath the bench as shown. By this method the support could be rigidly fixed in any desired position.

The electrodes consist of two brass cylinders, 2 cm. in diameter. These cylinders are held in ebonite sleeves, as depicted; the outside diameter of the sleeve is 3 cm. The lower sleeve is carried on an ebonite plate, whose height could be adjusted by the rack and pinion already referred to. The handle of this pinion is shown to the right of the lower electrode. To avoid sparking over the surface of the dielectric plate, the plate was cemented to the upper ebonite sleeve with sealing wax. It was not convenient to cement it also to the lower electrode, as when aligning the various components it is preferable to be able to remove the plate and the upper electrode. The slit can then be correctly aligned relative to the lower electrode by sighting through a small hole drilled in the film-holder for this purpose.

To supply the necessary voltage, we employed a large induction coil as a step-up transformer. The primary of the coil was supplied with A.C. current at 200 volts 50 cycles. By inserting suitable choking coils and resistances in the primary circuit, we reduced the primary current to about 2 amp. We found that this primary current gave a peak voltage across the secondary terminals of about 24,000 volts. This value is only approximate, as the only available method of measuring it was by the length of spark between spherical balls. It was found that using higher voltages generally either pierced the glass plate used as a dielectric or broke down the sealing wax insulation on the surface of the plate, and then sparked round the plate. When such a spark occurs, the primary current would, if allowed, run up to very large values and damage the coil. To prevent this we used a very light copper fuse in the circuit. The fuse blew at between 3 and 4 amps. In general, however, the total power consumed in the coil was small, about 40 watts, so that it was possible to run the coil for long periods without any tendency to overheat it. The thickness of the dielectric was about 2 mm., so that the potential gradient was about 120,000 volts per cm.

Photos 5 and 6 show two specimens of the results obtained. No. 5 was taken with the field on, and No. 6 with the field off. The slit was 0·25 mm. wide, and

the distance from the slit to the film was 24 cm. The length of the path of the γ ray in the glass plate was 3·5 cm., but the diameter of the electrodes could only be 2 cm., as otherwise sparking occurred over the edges of the plate. The exposure required was generally about 2 days with a fresh tube, and longer in proportion as the tube got older. The results were not as definite as might be desired, owing to the length of exposure required to give at all strong lines on the film. They fully proved, however, that no appreciable bending was caused by the field. In certain cases the image obtained with the field on appeared to be slightly wider, but usually this only occurred when this image was also slightly stronger, and the appearance of increased width is probably to be attributed to this greater strength.

We may, therefore, conclude that neither electric nor magnetic fields of the strengths available have any appreciable effect on the rectilinear propagation of γ rays.

We should like to express our gratitude to the staff of the Radium Institute of the Royal Dublin Society for the preparation of the radon capillaries, without which this series of experiments could not have been carried out.

PHYSICAL LABORATORY, TRINITY COLLEGE, DUBLIN,
March, 1929.

No. 22.

ON THE LOCAL APPLICATION OF RADIUM IN THERAPEUTICS.

II.—BI-RADIANT NEEDLES.

By J. JOLY, Sc.D., F.R.S.

[Read May 28. Published separately July 15, 1929.]

On March 24th, 1914, I communicated to the Royal Dublin Society a short paper *On the Local Application of Radium in Therapeutics.* The present communication is supplemental to the earlier one, its object being to suggest a special modification of the "Needle Technique"—as it is sometimes designated—enabling certain conditions to be attained whereby radiation of the desired character and strength may be applied to the malignant growth simultaneously with the application to the healthy tissues of such modified radiation as may be thought desirable.

I assume that such flexibility of treatment must, in some cases, be of value, seeing that not only are the tissues dealt with very different in character, but the effects sought for are by no means the same.

As regards the effects sought for, the Pathologist desires on the one hand the disintegration, solution, and removal of tumour cells as effectively as possible, the strength of the radiation being adjusted to these ends. On the other hand the healthy tissues (stroma cells) are to be stimulated to a defensive attitude against the spread of the malignant growth.

These conditions would appear to involve a certain degree of control of the radiations; the relative strengths desirable being ascertained as the results of experience. It does not appear that such quantitative estimates are at present available. Indeed, the efficiency of radioactive treatment of malignant conditions is generally ascribed to a selective effect naturally existing, which secures to the healthy cell immunity from radiations which are destructive of the malignant cell. The successful treatment of cancerous conditions, under existing conditions of radioactive administration, favours this view. While there are reasons for believing in the reality of such a selective effect, it by no means follows that such an effect may not be greatly enhanced if a method is available giving control over the distribution and strength of the radiations according as they are directed towards the malignant or towards the healthy tissues.

It is with the view of assisting in the obtainment of such differential radiation that the form of needle now to be described is suggested. A cross-sectional and

perspective view of a bi-radiant needle will enable its character to be at once understood (figs. 1 and 2).

The needle is bi-lateral. If we picture the ordinary hollow needle as divided longitudinally by a central plane, and formed of two semi-cylindrical halves composed of metals possessing different screening capacity, the nature of the bi-radiant needle will be at once understood.

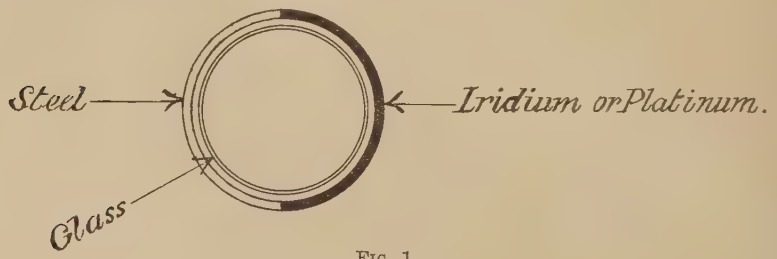

Fig. 1.

Plainly the rays proceeding from the opposing halves of the needle may be of very different intensity according to the nature of the substances selected to form the opposing halves. Figure 2 shows a combination of steel and platinum or iridium. The inner glass tube is used when radon is preferred as the source of the radiations. Again, a similar result may be attained by a structurally homogeneous needle, the bore of which is excentric; or, more generally, the outer form of which is such as to secure better screening of rays issuing over a certain segment than over the remaining arc of emergence.

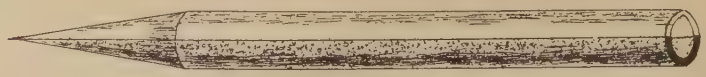

Fig. 2.

The radiations dealt with are essentially of two kinds only:—the β and γ rays, the α rays being stopped by almost any screening whatsoever. It is probable that β and γ radiations are, in their final effects, ultimately alike; the γ ray owing its efficiency to the β rays which are evolved attending its absorption in the tissues. Hence the ultimate therapeutic effects in all cases would appear to arise from ionisation within the living tissues.

Much valuable experimental work has been carried out on the absorption of β rays in their passage through matter. The co-efficient of absorption has been determined for many substances by Lenard, and found to be approximately proportional to the density. According to this relation the screening power of silver would be about half that due to platinum, the densities being 10·5 and 21·5 respectively. This result is confirmed by subsequent observations, especially by the work of Crowther (Phil. Mag. 12, p. 379, 1906).

If a bi-radiant needle is composed of halves having a like radial thickness, but formed of platinum and silver respectively, the radiations emitted from enclosed radium or radon will differ considerably according as they traverse the half needle composed of platinum or of silver.

We assume that the radial thickness of wall is 1 mm. On the platinum side there will be fairly complete stoppage of original β rays, whereas on the silver side the screening will be equivalent to what would take place through a platinum screen 0·5 mm. in thickness. This permits only a fraction of the β radiation, and, of course, a part of the softer γ rays, to pass through.

If such a needle is so located that the silver side faces inwards, *i.e.*, towards central parts of the malignant growth, the ionisation due to the issuing rays would be much the same in intensity and character as prevails in the case of the homogeneous platinum iridium needles favoured by Professor Regaud; the

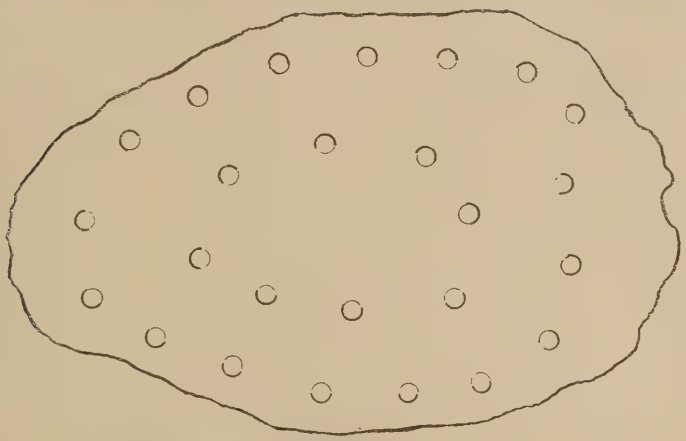

Fig. 3.

radial thickness of which is 0·4 to 0·5 mm., and which are used with radium element or, preferably, with radon. These needles are the standardised and perfected form of the needles as used in our Radium Institute since 1914—and as now developed by the distinguished Professor of the Pasteur Institute and Director of the Laboratory of Radiophysiology of the Institute of Radium of the University of Paris.

It is obvious that the opposed half-needles may be of different thickness, and in such a case may be composed of the same metal; the bi-radiant effect being entirely due to the radial thickness traversed by the rays.

The location of needles such as are now suggested would in general differ from the distribution assigned to needles radiating symmetrically. Their proper distribution would doubtless differ in different cases, and be determined in part as the result of experience. Of course the relative intensity of the two radiants may be more than is assumed in the foregoing case. It seems probable

that a linear arrangement of bi-radiant needles along and within the outer boundary of the tumour would be desirable; the needles being so orientated as to direct the strongest radiations inwards. Within this ring normal, mono-radiant needles might be distributed or further use made of bi-radiant needles; the feebler radiations being in each case directed outwards (fig. 3).

In the construction of bi-radiant needles features preventing a rotational movement must, of course, be introduced. There would be no tendency for such a rotational movement if the needles were slightly elliptical in cross-section, or, again, if the terminal point was replaced by a flat blade. A thin projecting fin traversing one or both sides of the needle longitudinally would also meet the end in view.

The construction of bi-radiant needles need present no special difficulty. The opposing halves may be formed in the first instance by planing such grooves in flat metal plates as will, when placed *vis-à-vis*, form the final cavity. Two such plates of the required metals, with grooves spaced accurately alike, being soldered or cemented together, may then be divided up, and each needle shaped externally into cylindrical or elliptic form, as may be desired.

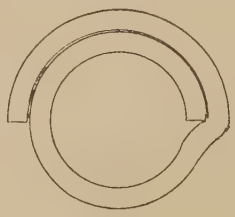

Fig. 4.

The simplest mode of construction, however, is to form the needle entirely out of platinum sheet, having a thickness of, say, 0·4 mm. A strip of this is rolled upon a smooth cylindrical rod, say of 1·5 or 2 mm. diameter. The sheet takes one and a half complete turns, and no more. The over-lapping part is soldered to the inner fold. The central rod is then withdrawn, and one end of the platinum tube closed by a turned steel or silver point, fitting and cemented into the tube. The walls of this needle are, evidently, for one-half possessed of a thickness of 0·8 mm. and the other half of 0·4 mm. The ledge on the surface where the outer fold ends will prevent a rotational movement.

It is probable that yet a different method of construction will be found more desirable. The ordinary platinum needle is first formed and completed with walls, say, 0·4 mm. thick. A strip of sheet platinum of the same thickness, and just so wide as to lap half-way round the needle, is then soldered along the entire length of the needle. This completes its construction.

It is hardly necessary to point out that any radial distribution of the rays—or number of differing radiants which special circumstances might call for—is attainable.

No. 23.

REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1928.

[Read JUNE 25. Published separately, JULY 31, 1929.]

HAVING regard to a recent statement in the public press respecting "Radium and Cancer," and referring to a "new technique" in radioactive treatment, the Committee deem it incumbent upon them to preface this Report with a statement respecting the scientific lines upon which the Radium Institute of the Royal Dublin Society has been conducted since its initiation in 1914.

The press statement to which we refer appears in *The Times* weekly edition (September 13th, p. 279). That journal is reporting an interesting statement made by Mr. T. W. Paulin as to the desirability of the London Hospital acquiring additional radium. In the course of this statement, Mr. Paulin refers to a "new technique" in the application of radium, which has given most encouraging results. He says:—

"The new technique, which has been in use on the Continent, at Brussels in particular, for some time past, consists in inserting a number of needles containing radium all round the cancerous growth—in favourable cases the growth is not only destroyed, but is prevented from spreading to the surrounding tissues."

It is not fair to give the credit of this technique to the Continent, as will be shown by the following:—

"In February, 1914, at the suggestion of Professor John Joly, the Science Committee recommended the Council to establish a Radium Institute, and to contribute a sum of £1,000 towards the purchase of radium. This the Council agreed to do."[1]

At this time reports from British and foreign institutions were coming in dealing with the use of radium and X-rays in the treatment of malignant growths; in many cases referring to the already recognised greater efficacy of radium treatment in dealing with cases of cancer.

As the result of a visit made at this time to the London Radium Institute and to the more important London hospitals by Professor Joly and Dr. Walter C. Stevenson, it became apparent to them that existing methods of radioactive treatment were in many respects defective; and a paper was communicated to the Royal Dublin Society, on March 24th, 1914, by Professor Joly, recom-

[1] See *A History of the Royal Dublin Society*, p. 377.

mending a quite new technique in the application of radium and its emanation in the treatment of malignant tumours. This paper clearly defines the suggested technique as having been worked out in conjunction with Dr. Walter C. Stevenson. This was the first suggestion as regards the treatment of cancer by radium emanation enclosed in metallic needles, and the entire credit must be awarded to Professor Joly and Dr. Stevenson. The aims of the suggested technique were essentially: (1) To give the surgeon more complete control over the distribution of the active rays, so that this might be approximately uniform, or concentrated locally, or in such other manner as might be desired; (2) to eliminate, as far as possible, the considerable wastage of radiations attending the heavy screening required with centralised dosage of great intensity, at this period in general use; (3) to eliminate risk of loss of the radium by rendering the use of the emanation (which embodies its therapeutic value) easy of distribution and sub-division, the parent element remaining in the laboratory.

This technique has become known as the "needle method," as it involves the use of hollow needles containing the radium itself, or, preferably, the emanation sealed in capillary glass tubes. The paper includes practical suggestions for the rapid preparation of these capillary receptacles uniformly charged with the emanation. Theoretical considerations respecting the economy involved are also included in this paper.

In January, 1915, Dr. Stevenson communicated a paper to the Section of Surgery of the Royal Academy of Medicine in Ireland, not only setting forth the theory and practice of the new technique in the clearest language, but supporting his statements by reference to recently obtained results. (See *Dublin Journal of Medical Science,* March, 1915.) This paper may be regarded as the first fruits of the technique introduced by the Royal Dublin Society. It most forcibly brings out the advantages attending the new method. The author instances a case wherein it became essential to control the spread in a particular direction of a growing tumour. A suitable distribution of the needles effected the object in view. Dr. Stevenson adds: "This systematic radiation of a growing edge is only possible by the use of the needle method, and is one of its great advantages."

The difficulties in dealing with the minute quantities of emanation abstracted from the dissolved radium were very considerable, involving work quite foreign to ordinary chemical routine. Valuable advice was received from the late Sir William Ramsay, F.R.S., but it is not too much to say that the voluntary work of Mr. R. J. Moss alone rendered the realisation of the aims of the Institute possible. In details, too many to recount, his inventiveness and resourcefulness smoothed over every difficulty. When he retired, in 1920, he left the Radium Institute, in every respect, a going concern.

This brief account of the aims of the Radium Committee, and how they were realised, will show how erroneous is the statement that the technique which this Institute favoured and supported from the first was of recent origin or

came from abroad. It was thought out and realised here in Ireland some fourteen or fifteen years ago.

We would be remiss if we did not, in this connection, acknowledge the sources from which came the financial support which enabled the Institute to accomplish its work.

The capital outlay required for the purchase of radium was, as might be expected from the high price of radium, very considerable. The Council of the Royal Dublin Society voted £1,000 upon the foundation of the Institute. The late Earl of Iveagh and Sir John Purser Griffith contributed £1,000 each. From these sources the Radium Committee was able to acquire 110 mg. of radium element. Adding to this a quantity of 30 mg. of radium already in the possession of the Society, the total came to 140 mg. This was increased in 1920 by 220·6 mg. of radium element lent by the British Government upon the intercession of Sir Edward Coey Bigger, chairman of the Radium Committee. Subsequently a further 50 mg. of radium element were purchased out of the proceeds of the sale of an old laboratory stock of platinum dishes.

It will be seen that the total amount of radium element in the possession of the Radium Institute is only some 410 mg. We wish to emphasise the fact that this is not nearly enough to meet the requirements of Ireland. The applications have generally to be deferred till earlier ones are attended to. Such delays may be of serious import in the treatment of cases of malignant disease.

During 1928 a modified form of apparatus has been devised and constructed for the preparation of the radium emanation capillaries supplied to medical users. The original apparatus, which was the first of its kind in the world, had been in constant use since 1914. The new modification is of a semi-automatic nature, and enables the various operations to be carried out with much less exposure of the operator to the radiations. It also requires less skill in manipulation, so that a change of operators can be made at intervals sufficiently short to prevent all risk of injury. During the experimental work necessary in the construction of the new apparatus the available supply of emanation was somewhat restricted. Chiefly as a result of this, the amount of emanation issued for medical use was only 12,111 millicuries, as compared with 14,306 millicuries in 1927.

During the year two Exhibitions of £50 a year each were established. These exhibitions, which are tenable for one year only, are open to Science and Medical Students of Trinity College and University College, Dublin. The holders attend at Ballsbridge for a couple of hours twice a week, and assist with the work of the Radium Institute, thus relieving the permanent staff from risk of injury from the cumulative effect of prolonged exposure to the radiations, and, at the same time, acquiring a practical knowledge of the method of handling radium emanation. The competition for these exhibitions was very keen, the successful candidates being Mr. Denis Crowley and Mr. W. J. E. Jessop.

Report for the Irish Radium Committee (Royal Dublin Society) of Radium work carried out in the year 1928.

By Walter C. Stevenson, M.D., B.Ch., D.P.H.,
Surgeon, Dr. Steevens' Hospital, Orthopædic Hospital, etc.

Cases Treated with Radium.

List showing number of patients and the conditions treated during 1928:—

Malignant Cases, 101.

Cancer of Breast	8
Cancer of Uterus	15
Body, 1; *Cervix*, 14.	
Cancer of Vagina	4
Cancer of Nose and Mouth	23
Palate, 1; *Tongue*, 15; *Floor*, 6; *Lower Jaw*, 1.	
Cancer of Larynx	2
Cancer of Pharynx (Extrinsic Larynx)	3
Cancer of Oesophagus	2
Cancer of Stomach	1
Cancer of Sigmoid	1
Cancer of Rectum	3
Cancer of Neck	1
Cancer Root and Neck	2
Cancer of Skin	16
Cancer of Lip	6
Sarcoma	5
Melanotic of Conjunctiva, 2; *Maxillary Antrum*, 2; *Clavicle*, 1.	
Rodent Ulcer	9

Non-Malignant Cases, 120.

Abdominal Adhesions ...	5	Dupuytren's Contraction ...	1
Abscess	2	Furunculosis	1
Blepheritis	2	Fibroma (Bleeding)	2
Caeliac Disease	2	Fibrosis Uteri	2
Carbuncle	1	Fissure, Lip	1
Chilblains	1	Gastric Ulcer	1
Colitis	2	Glands, Inflammatory ...	5
Cyst	1	Goitre, Exophthalmic ...	3
Deafness	3	Injury	9

NON-MALIGNANT CASES—*continued.*

INFLAMMATION	...	...	2
KELOID	...	...	1
LEUCOPLACIA	...	...	1
LICHEN, PLANUS	...	...	1
MENIER'S DISEASE	...	...	1
NAEVUS	...	...	3
NEURITIS	...	...	1
NERVE INJURY	...	...	2
OTORRHAEA	...	...	1
PAPILLOMA, LARYNX	...	...	1
PARONYCHIA	...	...	2
PNEUMONIA (HYPOSTATIC)	...		1
PROSTATE (ENLARGED BLEEDING)			1
PSORIASIS	...	...	1
PYORRHEA	...	...	2
RHEUMATISM	...	...	2
SCIATICA	...	...	6
SCARS	...	...	2
Septic, 1; *Painful*, 1.			
SEPSIS, ACUTE	...	...	2
SEPSIS, CHRONIC	...	...	3
SEPTIC NODULES	...	...	2
SINUS	...	...	3
Bone, 1; *Ischio-Rectal*, 2.			
SORE THROAT	...	...	1
SPASM, TENSOR TYMPANI	...		1
SYCOSIS	...	...	1
TONSIL (CHRONIC INFLAMMATION)			1
TRACHOMA	...	...	1
TUBERCULOSIS	...	...	25
Abscess, 1; *Abdominal*, 1; *Bone*, 1; *Larynx*, 2; *Lung*, 1; *Joint*, 1; *Lupus*, 1; *Lupus Erytematosis*, 1; *Otitis Media*, 1; *Peritonitis*, 13; *Sinus*, 1; *Spine*, 1.			
ULCERS	...	...	3
Gunshot wounds, 2; *Varicose*, 1.			
WARTS	...	...	2

Total number of Cases treated ... 221.

In reference to the actual cases treated this year, I do not propose to enter into details of doses, as I did in the 1926 report, or technique, as I have done in 1925 and 1927, but to give a general idea of the results obtained.

Most of the patients treated for malignant disease were sent to Dr. Steevens' Hospital for radium treatment from the country or from other Dublin hospitals, when nothing else could be done for them. It is astonishing how advanced some cases of malignant disease are, with large tumours, ulceration, and extensive involvement of glands, before they come for treatment, so that it almost seems a waste of energy doing anything for them, when a cure cannot possibly be expected. These patients could not stand the dose necessary for a radical treatment, nor can they stand the shock of combining operation with radiation. My idea in treating such patients is to relieve their symptoms, a result which I am usually fortunate in obtaining. In doing this work I have completely disregarded the reputation of radium as a cure for cancer, as this can stand on its own merits.

I may mention that some patients have died before I could undertake their treatment, and, in other cases, I have had to stop the treatment, as I saw that it would take too much out of the patients, who were already profoundly toxæmic. Frequently I combine operations with radium treatment, as in so-called inoperable, or border-line, cases of cancer of the breast. In these cases

the cancerous mass is removed with the gland in the axilla, but a complete Halstead, with removal of both pectorals, is not performed. Radium tubes are inserted into the axilla at the operation, and removed in a few hours to a couple of days, according to the radium I have available at the time, and the pectoral region, the line of the operative scar, the axilla, and the supra-clavicular region are given surface radiation when the operative wound has healed. Though small doses stimulate the healing of a wound, cancer doses tend to delay it, especially when the vascularity of the skin is diminished by the operative procedure.

I also find that the axilla immediately after operation will not stand the amount of radiation I frequently employ by burying needles and tubes in a malignant growth. As I have pointed out in various papers—first in March, 1915—a tumour itself is not usually a matter of vital importance, but it is the extension into the surrounding parts that leads to fatal results, and it is often astonishing what big doses a tumour will stand without untoward effects. I regard a tumour as a convenient holder for radium tubes, or a pin-cushion for needles, and what one really aims at is the efficient treatment of the surrounding edges. My idea is to use the tumour as an efficient screen or filter for the surrounding healthy tissues, so that they may be enabled to resist the advance of the cancer. With this technique the tumour shrinks, sometimes being replaced by a fibrous mass, while the surrounding reaction has the best chance of staying the progress of the disease.

The disadvantage of an annual report, which only deals with the cases treated during one year, and is made out shortly after the termination of that year, is that it does not give any indications of the permanent cures, as far as cancer is concerned. Naturally, some of the very advanced cases will have died during the year, which, unfortunately, is little indication of the usefulness, or otherwise, of the radium treatment of cancer. The position is somewhat analogous to tuberculosis; in spite of our knowing so much about the latter disease, the annual deaths from tuberculosis, though diminishing, are fairly extensive. The more one sees of cancer the more one realises that no treatment can effect a cure in some cases, as no treatment appears to be able to effect a cure in some cases of tuberculosis, but that radiation, sometimes combined with operation, is one of the most efficient methods of treating cancer, there is no doubt.

Though the treatment of cancer by successful operation, and more particularly by radiation, may have the effect of increasing an individual's resistance to the cancer tendency, there is not sufficient evidence to prove this. It is, however, significant that there are many cases in the literature of cures of five and ten years' standing by radiation in inoperable cancers. At the same time, operation and radiation are mainly a local treatment. Any constitutional treatment, therefore, which is proved to have a definite effect in curing cancer, without taking too much out of the patient, would be a great boon, especially as early

metastases cannot be detected. I was, therefore, in this connection, struck by the guarded account which Dr. Todd, of Bristol, gave me while in London of his recent work with the intravenous injection of selenide of lead for the treatment of cancer, and determined to try it as an adjunct to radium treatment. Most of the injections have been given by Dr. Townsend, House-Surgeon of Dr. Steevens' Hospital, and the results so far encourage me to persevere. We have administered the injections some weeks after the last treatment, using 2·5 to 3 c.c. about every fortnight, or less than a quarter of the dose recommended by Dr. Todd. As the lead is injected some time after the administration of radium, the idea of the treatment has not been to sensitize the tissues to radiation by the secondary rays given off by lead—an idea which also appeals to one—but more for its tonic effect, and possible specific action on malignant cells. In one case of cancer of the tongue it appeared to hasten the healing of the ulcer, which was slow in completely healing after radium treatment. In another profoundly toxæmic case of cancer of the floor of the mouth, the malignant nodules appeared to get smaller, but the patient succumbed to the toxæmia, which in time would have been fatal in any case, as his disease was very advanced.

Some of the other cases in the same category have also died, and the treatment has been administered to a few where radium treatment has already resulted in an apparent cure, as it appears to me to be a sound prophylactic measure to adopt.

Radium treatment never can be a routine method, as the cases in themselves differ, and no two cases of cancer of the tongue, for instance, are exactly similar, either in the locality of the disease, the extent of involvement, the amount of tumour formation, the extent of ulceration, the involvement of neighbouring structures and glandular infection, &c., so that the part to be treated varies considerably, and a dose that would be suitable for one case might not give a good result in another.

Not only the local condition has to be considered, but also the age of the patient, his general health, and the amount of toxæmia from which he is suffering.

When radium salt is used, the amount of radio-active material is constant, and with the same platinum needles the amount of screening is also constant; but the intensity of radiation per unit of time depends upon the relative distance of the needles from one another, and the dose required depends upon what one aims at in the treatment. For instance, when there is a great deal of tumour formation which requires to be destroyed, a larger dose is usually necessary, and can be tolerated, than in the case where there is not much redundant tissue and induration. When radon is used, however, the radio-active material present is seldom the same in intensity per capillary, or in the total amount of millicuries present, and of course its activity is constantly decreasing; the only constant entity is its proportional rate of decrease.

In order to facilitate the work of recording the treatment, I drew up last

year, and now use, a large two-sheet printed radium chart, folded to make eight pages. The outer sheet, page 1, is devoted to particulars of the patient and the disease, and page 8 to the history and details of the disease: for instance, size of ulcerated area, histological reports, &c. The actual details of the treatment are recorded on pages 2 and 7, considered as one sheet. The upper half of this sheet is blank on page 2 for the diagram of the part treated, and on page 7 is printed the radium emanation table, which gives the hourly loss of from 1,000 to 100 millicuries, arranged in thirteen 24-hour columns. By the use of decimal points this table is applicable to any quantities of radon.

In making the diagram, the part treated is outlined in ordinary ink; green ink indicates the diseased areas, and red ink the radium, violet ink being used for apparatus, where necessary for clearness. My crude sketch does not take two minutes, but in this way it is possible to see at a glance the locality and the nature of the treatment that has been employed.

The lower half of this sheet is divided into 22 columns, under various headings. These give:—

Locality of treatment.
Nature of treatment (buried, internal, surface).
Hours and dates treatment started and finished.
Agent employed (whether radium or radon).
Serial number of the radon supply.
Activity of the radon when each detail of treatment is started and when it is finished.
Amount of radon disrupted (med.), or loss of activity during treatment (which can be read off from the table immediately above in the case of radon, and is constant per hour for a supply of radium).
Number of hours which treatment lasted.
Filter used.
Volume radiated in c.c.
Number of foci employed.
Distance of the radium or radon from the nearest cells in mm.
Distance piece employed (whether of felt or other material).
Med. (millicuries disrupted) per c.c.

Pages 4 and 5, the centre of the second sheet, are devoted to instructions. The upper half bears general instructions for all cases, explaining the care that must be exercised. The lower half is divided into columns showing:—

The part of the body to be treated.
The hour, day, and date when treatment is to be commenced.
The number of hours that it is to occupy.
The time it is to finish.

This page is filled in by me when the details of treatment have to be

carried out in my absence: for instance, at 4 a.m., by the night sister in hospital. As each detail is carried out, it is entered on page 2, already described, and signed in the proper column by the person who carries it out. These precautions are necessary to ensure accuracy and to prevent the work from being done in a haphazard manner. All instructions are given in absolute detail, so as to avoid any chance of misunderstanding, and the diagram helps to show what has to be done.

Page 3, the outside of the second sheet, is divided into three parts for further details of treatment; one part deals with surface treatment, a second part with internal treatment, as when a tube containing radium is inserted into a natural cavity, like the œsophagus or uterus. The third part is devoted to buried treatment, and gives particulars of the lengths of the needles used, the distance they are inserted, and the distance extension pieces project, that is, the relative position of the radium to the skin or surface at any stage of the treatment.

Page 6 is blank for notes on history, treatment, and effects of the case.

By using this form I am able to get details of treatment recorded very much more easily and promptly, which is of the utmost value in obtaining a reliable and systematic record of a treatment.

The following is a brief record of some of the results obtained in malignant diseases during the year. One cancer of the breast, and possibly two others, are apparently well after operation and radium treatment. In another patient, aged 81, a growth, which was inoperable on account of the patient's age and chronic bronchitis, completely disappeared, and a clinical cure was obtained, the patient succumbing to bronchitis in the winter, five months after the treatment.

The second patient who died had recurrence soon after operation in a Dublin hospital; she had several nodules and a distinct tumour of one of the ribs. These completely disappeared after the radium treatment in May, 1927. On account of pain about the shoulder and chest, she was again treated in March, 1928, but died in December, rather quickly, with head symptoms, which her surgeon considered were due to metastases in the brain.

In inoperable cancer of the uterus this year, the results have been gratifying, though three very advanced cases died comparatively soon after treatment. The short exposures it was only possible to use cannot be considered to have hastened the fatal termination. In two of them there was temporary relief of symptoms. Three others, as far as one can judge, were cured. In most cases of cervical cancer, as described in previous years, I radiate the uterus and cervical canal by one tube pulled into three positions. This can be done quite accurately by securing the wire extension, which has been screwed into the tube and is marked in centimetres, in a special clipping apparatus, which is firmly fixed to the perineum by strapping and two pieces of tape. By knowing the radio-active length of the tube and measuring on the wire the length the tube can be inserted into the uterine cavity from the lower limits of the growth,

and noting the length of wire that projects beyond the clip when the tube is at the top of the uterus, the relative position of the radium to the uterine cavity and cervix can be determined at any time during the treatment.

I commonly employ a dose of about 30 mcd., equal to 4,000 mg.-hours. Usually this dose is sufficient to obtain a satisfactory result. As the dose is fairly big, I have hesitated to use at the same time a flat applicator, applied to the surface of the os in addition, when it is possible to get the tube to the fundus of the uterus, on account of the risk of injuring the bladder and rectum, unprotected by the thickness of the tissues of the uterus.

I wish particularly to report one case (treated at the Rotunda Hospital for the Master, Dr. Solomons), where, in spite of a full uterine dose, I used at the same time two brass boxes (filter 3 mm. brass, plus rubber), containing radon capillaries, the radiating area of each being 3 × 2 cm., packed against the face of the cervix with gauze, the wall of the vagina being at the same time distended by an aluminium distance tube of 3·3 cm. diameter, to push away the bladder and rectum. The whole treatment lasted 72 hours, the tubes being pulled out 2 cm. every 24 hours, while the boxes were undisturbed. During this time the radon in the boxes was reduced from 48·6 to 28·3 millicuries, *i.e.*, a dose of 20·3 mcd., while 53·93 mg. of radium element were used in a brass tube, 10 mm. in diameter and 3 mm. thickness of wall, which I employ when possible in these cases. This gave a dose of 28·8 mcd. in 72 hours.

This patient, therefore, received a total dose of 49·1 mcd, or 6,547 mg.-hours, at one sitting. Twelve days after the treatment she suffered from violent tenesmus and diarrhœa, which were completely relieved in two or three days by injections of bismuth in mucilage. She had no further rectal trouble. Nine weeks after the treatment the patient returned to the Rotunda with some occasional hæmorrhage, but otherwise very well, and, as the case was now operable, Dr. Solomons removed the uterus. Apparently the operation presented no difficulties from hæmorrhage due to excessive vascularity of the part, or from the fibrous tissue that had resulted from the radium treatment. The following is the histological report of Dr. Burke, the pathologist:—

Report on Uterus from Mrs. K. K.

Clinical History:—Wertheims' Hysterectomy after Radium Treatment.

Naked-eye.—The uterus was normal in size; it was opened by a mid-line incision. The cervix felt rather hard, and was whitish in colour; towards the external os the cervical tissue sloped forwards, to merge with the wall of the vagina, so that it was impossible to say where the cervix ended and where the vagina began; the fornices were obliterated. The adnexa were normal, and there was no noticeable thickness of the parametrium.

Microscopic sections were made from the anterior and posterior walls of the cervix, from the fundus uteri, and parametrium. There is no evidence of malignant disease to be found in the cervix or uterus.

There are scattered areas of round cell infiltration all over the sections, particularly marked in the superficial tissue of the cervix, similar to the appearance I have often seen in malignant disease after radium.

The muscle wall shows a good deal of hyaline change, and there is a large nodule of hyaline material, with free blood in it, to be seen in the cervix, near its junction with the vagina. The glands show no abnormality. There is a considerable increase in the connective tissue in the wall of the uterus. The sections of the parametrium show hyaline change occurring in the walls of the larger blood vessels; there is no evidence of malignant disease.

This case is of particular interest to me in indicating the effect of radiation on operative procedure in uterine cancer, as some guide to the best time to operate after radiation, and as showing the manner in which the total dose in a cervical case may be increased at one treatment without undue risk to the surrounding parts. If the operation had been performed three weeks after radium treatment, the patient might have died of shock; in six weeks there would probably have been more hæmorrhage, and in six months it is quite likely that there would have been considerable difficulty in removing the uterus, on account of the amount of fibrous tissue which had become organised after radiation.

I think it quite likely that, in the above case, if the same dose had been given in 24 hours instead of 72 hours, by using three times the amount of radioactive material, or if the vagina had not been well distended by gauze and an aluminium distance tube, the rectum might have suffered permanent damage.

As a matter of fact, in a number of cases of cervical cancer treated by me, the disease is so advanced that it is impossible to give a really large dose, as the tube cannot be got into the uterus without undue risk, and one is limited to one or two *foci* of radiation instead of four. This must of necessity decrease the dose by at least a half, and sometimes more, as I regard the uterus as a most efficient screen for protecting the surrounding structures. Unfortunately in such cases it is usually difficult to arrange for a series of treatments at intervals of three weeks, as the patients will not attend, especially when they come from the country.

In one of the other cases, in which I was inclined to give a bad prognosis, and which appears to have done very well, there was a pyometria of the uterus, which was curetted immediately before inserting the tube. The same technique was used in the uterus with a dose of 26·8 med., or 3,500 mg.-hours, but a surface dose was also administered over the pubes, sacrum, and anus of 25·3 med.

One case of ulceration and cancerous growth in the anterior wall of the vagina practically cleared up by a week's treatment with a brass box in a finger-stall containing 7·5 mc., a dose of 5·4 med., the rectum being protected by a plug of gauze and a lead plate covered by rubber. Five months later the

two small remaining nodules were treated by the insertion of six needles for five hours, dose 2·0 med.

Of the cases of cancer of the tongue and palate, five very advanced cases have died; two are apparently cured, possibly three; two have been lost sight of; and the remainder are doing well, but are too recent to pronounce judgment on.

One case of cancer of the larynx, with post-operative recurrence in the glands, Mr. T. O. Graham reports, has apparently been cured, and in three cases of cancer of the pharynx the disease has been markedly checked, but the ultimate results are not hopeful. Four cases of cancer of the lip have apparently been cured; also four of cancer of the skin, which have been traced.

Of the sarcomata, two with small melanotic growths in the conjunctiva, and one with a growth at the inner end of the clavicle, have apparently been cured, while two rodent ulcers are also known to be cured, to all appearances. A number of the other cases, which are not mentioned in detail, have probably succumbed to the disease, as they were in an advanced stage when the treatment was undertaken. It is impossible single-handed to follow up all these cases, but, occasionally, one is surprised to hear from other sources that patients, whom one would expect to have died years ago, are still alive. For instance, I heard recently from a fellow-passenger in a tram that a case of inoperable sarcoma of the nose and naso-pharynx, which I reported in the *Medical Press and Circular*, December, 1915, is still in robust health, and working in Guinness's Brewery. Similarly, a case of inoperable sarcoma of the uterus, clinically and microscopically, which was treated in February, 1926, consulted her specialist, Dr. Gilmor, for recurrent pain in the pelvis. On his examination he found a tumour present, and, as the patient did not wish to have further radium treatment, and appeared now to be in a fit condition for operation, her abdomen was opened, and a cystic tumour of one of the tubes and of an ovary, each about the size of a large pear, were removed by him. The uterus had shrivelled up, there was no appearance of malignancy in any part, and the tumours proved to be simple cysts containing fluid, so that this case may be considered as an apparent cure.

As for the non-malignant cases, it has been pointed out in previous years that their treatment in no way interferes with the treatment of malignant disease, for the specific purpose of treating which some of the radium held by the Royal Dublin Society was granted by the British Cancer Research Committee. For all practical purposes radon supplied by the R.D.S. and the radium which I have bought would often be wasted if not used for non-malignant cases. Indeed, in a few cases, the whole treatment, usually with β rays only, lasts a minute or two, while, in a number, less than a total of one millicurie is employed, contained in a dozen capillaries which would otherwise be discarded. Besides, when radon was supplied by the R.D.S. in 1914, it was with the idea of investigating its effect on disease generally, and not only on cancer in particular, so that practically from the start I have been using radiation for non-malignant

cases. I used it extensively during the latter years of the war and until 1925 for the treatment of disabling scars due to gunshot wounds. In many cases of amputation the patient was enabled to use an artificial limb, which the painfulness of the stump prevented him from doing before the treatment, and marked functional improvements of other disabled limbs were obtained. Perhaps the most gratifying results in non-malignant conditions have been achieved in the treatment of tuberculous peritonitis. At least two cases, which had been given up by consultants, have made complete recoveries, and the convalescence in a number of cases has been markedly shortened and followed, in a comparatively short time, by a return to normal health. The first two cases were treated in 1921, and recorded in the *Dublin Journal of Medical Science,* February, 1922. Sixteen patients were treated from 1921 to 1926 inclusive, eight in 1927, and twelve in 1928. The two original cases are in perfect health, though one of them had a tuberculous elbow as well, which has been cured with the help of radium. Several of the patients had been operated on, and the local condition found to be extensive, and had not improved till the radium treatment was applied, when their symptoms were almost immediately relieved, and in about three months' time they seemed to be well. The above account of the number of patients who in various years have been treated for T.B. Peritonitis shows that in Dublin, at least, the efficacy of this method of treatment has become recognised, though it does not appear to have been tried in London. I believe radium has a great advantage over X-rays in tuberculous conditions, as the dose can be administered much more gently. For instance, one of the worst T.B. Peritonitis cases which recovered had radium treatment for 54 days, while, incidentally, a case of tuberculosis of the lung, with extensive hæmorrhages, had, as a final radiation, 2 mg. of radium continuously for seven months. This last patient was over four years in Dr. Steevens' Hospital, and when last seen, about a year later, had become fat and appeared to be in robust health.

When one considers the marked effect on cancer cells as seen by the microscope six hours after insertion of radium needles (Morson), one has to admit the powerful effect radiation has on the metabolism of cells. In all inflammatory conditions the cells of the inflamed part are at a disadvantage, and radiation, especially in small doses, must affect the metabolism, and, in my experience, it does so beneficially, and helps the tissues to return to normal conditions. Radiation, in fact, acts as a very efficient and scientific linseed poultice, and anybody who has had heat applied to a painful or inflamed part will appreciate the comfort that follows. For instance, one of my residents had a very swollen, inflamed and painful throat, and expressed a wish to have radium treatment. In two or three hours all the pain had gone, and, as he expressed it himself, "it felt so funny to have a big lump in your throat, and not to feel any discomfort from it." I have previously described how a diffuse inflammation of the throat, which looked as if it should have been opened, subsided quickly following mild radiation.

Of course, a number of these cases would not be treated with radium only that it is available, but the experience gained by such treatment is valuable in dealing with more serious conditions, for instance, ulcerated cancers, where septic con-

ditions play an important part in the progress of the disease. Similarly, one has frequent ocular demonstration of the effect of radium treatment on lupus and on scars, so it cannot be doubted that radiation has some effect on all tuberculous conditions such as those mentioned in this year's report. As scars on the surface are visibly affected, it is reasonable to expect that abdominal adhesions have some chance of stretching, and the parts of freeing themselves, after radiation, which must be very thorough. As a matter of fact, the constipation and pain were decidedly relieved in cases treated during the year. One case of marginal blepheritis, which would not respond to prolonged treatment of various kinds, got well after mild radiation, and it appeared to do great good in two cases of mucus colitis. Two cases of fibrosis uteri were cured. Hæmorrhage, which had continued for a long time, ceased in a case of gastric ulcer, as also did the bleeding in an enlarged prostate, which had not been amenable to various forms of treatment. One of the cases of sciatica had suffered for seven years, had been to various watering places, had been operated on, and had had the nerves stretched with only a very temporary benefit. This patient has not been completely cured, but is steadily improving, and states it is the only treatment which has given her any relief. The results with sciatica are, on the whole, very satisfactory. One case of exophthalmic goitre did very well, in the second there has been considerable improvement, in the third the effect has not been, so far, marked. A case of Menier's disease was treated for 48 hours with an initial dose of 7·08 mc. in a brass box over the mastoid, and for three hours by a 9 × 9 cm. applicator at a distance of 25 mm. with 140 mc. This stopped the patient's headaches and the buzzing noises in the ear, and he expressed himself as greatly benefited by the treatment. The improvement in vertigo, headache, and sickness to which he was subject appeared to be maintained when he was last heard of, four months later.

A case of spasm of the Tensor Tympani, which had persisted for some years and greatly interfered with the patient's concentration of mind (he was a doctor), was improved almost immediately after treatment, and about four months later the patient reported this rare condition as 95 per cent. improved.

One case of trachoma, involving the cornea, was virtually well when last heard of. In one case of septic nodules, the sequelae of severe puerperal sepsis, the painful nodes on the soles of the feet and the back of the heels, which got almost a full cancer surface dose, disappeared, while other spots which had got smaller doses were not so markedly improved.

In practically all the cases treated the results justified the method employed, and treatment of most of the conditions had been undertaken as they had proved intractable to the routine methods.

In conclusion, I desire to express my indebtedness to Dr. Poole and the staff of the Royal Dublin Society for their invaluable help and consideration for my requirements when supplying radium emanation. I appreciate especially the kindness of those who have asked me to co-operate with them in radium treatment of their patients in special branches of surgery, and wish to thank my residents and nurses at Dr. Steevens' Hospital in loyally carrying out the work there.

Report on Seventy Patients treated by Radium during the year 1928.

By M. R. J. Hayes, F.R.C.S.I.

Seventy patients were treated during the year 1928. These comprised twenty-eight which were malignant, and forty-two which were of a non-malignant character.

Malignant Cases, 28.

Breast	4	Uterus	2
Oral Group	14	Epithelioma of Skin ...	6
Lip, 6; *Floor of Mouth*, 2; *Tongue*, 2; *Fauces*, 3; *Antrum*, 1.		Sarcoma of Skin	1
		Fibro-sarcoma	1

Non-Malignant Cases, 42.

Rodent Ulcers	28	Vernal Catarrh	1
Warts	7	Lingua Nigra	1
Moles	2	Lupus Verrucosa	1
Cavernous Angioma	1	Lupus Erythematosus ...	1

Mammary Cancer.

Three were primary and one was recurrent. Of the three primary cases, two were operable, but the patients objected to operation. The third suffered from chronic asthma and fibroid phthisis, which were contra-indications to operation.

Each had a primary growth in the breast, with enlarged axillary glands. In one the primary growth had ulcerated. Clinically, all were of the scirrhus type of carcinoma; histological examinations were not made. In each case five needles (·4 mm. platinum, ·3 mm. gold), each containing from 5 to 10 mc. radon, were embedded circumferentially around the primary growth, and left *in situ* until 2 mc. per c.c. of neoplastic tissue were dissipated. The axilla and supra- and infraclavicular regions were treated by deep X-rays, 110 per cent. D.D. being given in divided doses over a week. The immediate result has been retrogression of the growth, and of the enlarged glands in all the cases treated.

Carcinoma of the Lip.

Five primary. Growths small and superficial; ulceration slight; no enlarged lymph glands. All received surface applications through 2 mm. aluminium, 60 mc. h. per sq. cm.

One case, which recurred two and a half years after excision, was treated by combined needling and surface applications.

As a routine the submaxillary regions in all these cases were treated by deep X-rays. Ulceration has been replaced by a healthy scar, and there is no disfigurement. The recurrent case died suddenly from heart disease eleven months after treatment, but when he was seen after four months his carcinoma had disappeared. One patient who had recurrent carcinoma of the floor of the mouth is still under and responding to treatment. Another very advanced case is not improving.

Carcinoma of the Tongue.

Two cases treated by implanting needles are very much improved, but sufficient time has not elapsed to forecast a final result.

The writer recently saw a patient whom he treated with radium for carcinoma of the tongue in December, 1927. The disease then involved the anterior half and the right side of the tongue, and its under surface was ulcerated. It was almost fixed, and articulation was difficult. The tongue is now normal; nothing is to be seen except the scar of the original ulcer. There is, however, a recurrence in a gland beneath the sterno mastoid at the level of the lower border of the thyroid cartilage, which was apparently outside the field of the deep X-ray treatment, which was applied to the submaxillary region in 1927.

Carcinoma of Fauces.

In two cases ulceration had healed, and there are no manifestations of the disease. One who is a chronic alcoholic and would not co-operate is not improving.

One advanced case of carcinoma of the antrum (aged 73), who was first treated in 1927, was greatly relieved by applications which were given from time to time for more than a year, and the disease was definitely kept in check. Death ensued from œdema of lungs.

Carcinoma of Uterus.

One very advanced case of carcinoma of the cervix was treated in January, 1928. Before she left hospital discharge and hæmorrhage had ceased, and the local condition was very much improved. No recent report. One case, also very advanced and inoperable, was first treated in October, 1927, and she was free from symptoms until July, 1928, when she returned to hospital, complaining of severe pelvic pain. On examination, the anterior and posterior vaginal walls were adherent and forming a thin septum, which was easily penetrated by a sound. The uterus was not enlarged, but there was some induration around the cervix. There was no evidence of ulceration. General condition very good. Radon was again applied in July, 1928. No recent report. The technique applied in the treatment of these cases is similar to what has been described in my previous reports. The amelioration which radium therapy gives to these cases, which are otherwise utterly hopeless, is inestimable.

Cutaneous Epithelioma.

Six cases have been treated during the year, and in all the ulcers have healed.

Sarcoma of Skin.

This condition developed in a traumatic ulcer of the skin, which was irradiated many years ago, when the patient was suffering from Graves' disease. The ulcer was excised, and the diagnosis was based on histological examination. Recurrence followed excision of the ulcer, but it healed after surface applications of radon filtered through 2 mm. brass, 1·5 cm. distance, 9 millicuries dissipated.

One patient, who had fibro-sarcoma of the thigh, was not improved.

Rodent Ulcers.

Twenty-eight cases were successfully treated after the manner described in my previous reports.

None of the other miscellaneous group of non-malignant cases deserves comment, except, perhaps, one patient who suffered from a rare disease, viz., Lingua nigra. A surface application of radon, 23 mc. 2 mm. al. 5 minutes, was given the first day. Next day, 59 mc. 2 mm. al. 5 minutes. The third day, 51·5 mc. 2 mm. al. 5 minutes. A month later the patient reported that his tongue was quite normal.

In concluding, I have to thank Dr. Poole and his assistants at the Institute for their unfailing courtesy to me at all times.

No. 24.

PHOTO-ELECTRIC MEASUREMENTS OF ILLUMINATION IN RELATION TO PLANT DISTRIBUTION.

Part II.

MEASUREMENTS WITH PORTABLE GALVANOMETERS.

By W. R. G. ATKINS, Sc.D., F.R.S.,

AND

H. H. POOLE, Sc.D.

[Read May 28. Published separately August 23, 1929.]

In a previous paper (1926) we described measurements of illumination carried out with an apparatus which had been designed primarily for use on a ship for determining the submarine illumination. This was amply sensitive for work on land, but its bulk and weight constituted a serious drawback. We accordingly sought to use portable galvanometers as measuring instruments, in combination with various photo-electric cells. The difficulty of doing this consisted in the fact that the potassium vacuum photo-electric cell which we used previously was not sensitive enough to give conveniently large deflections when used with a portable galvanometer in shaded sites.

We accordingly had recourse to a gas-filled cell. This contained caesium, which was chosen on account of its high sensitivity to green light. The spectral sensitivity of this and other photometers used has been given in another paper (1928). The drawback of using a gas-filled cell is that is does not give a constant reading for a given intensity of illumination, and so it must be calibrated frequently against a vacuum cell.

Measurements were made in the autumn of 1927, using the vacuum potassium cell, photometer H, and the gas-filled caesium cell, photometer C, both mounted beneath diffusing surfaces of ground glass.

As a measuring instrument, a Tinsley portable galvanometer was used. Some of the results obtained with this outfit are recorded in Table 8. Most of the measurements made in 1927 have, however, been disregarded as of doubtful accuracy, since we were able, in 1928, to assemble apparatus which gave accurate results, and was altogether more convenient. The 1928 measurements were made with Burt vacuum sodium photo-electric cells. Since these give a very

large current as compared with photometer H, and are of similar constancy, their adoption marked a great advance; their high sensitivity, moreover, enabled more robust measuring instruments to be used.

Optical Conditions.

In our 1926 paper we defined the vertical illumination as the illumination, in metre candles, falling on a horizontal surface. This is what is generally measured by the photometer when certain small corrections have been applied for reflection losses at the front faces of the glass windows. It is denoted throughout by the letter *V*. Another definition, which is very useful in photometric work in woods, is the illumination in metre candles of the surface set to catch the maximum amount of light. We will call this the maximum illumination, and denote it by the letter *M*. For a further consideration of the optical conditions reference may be made to the former paper, which also contains a table showing the reflection-loss factors by which the photometer

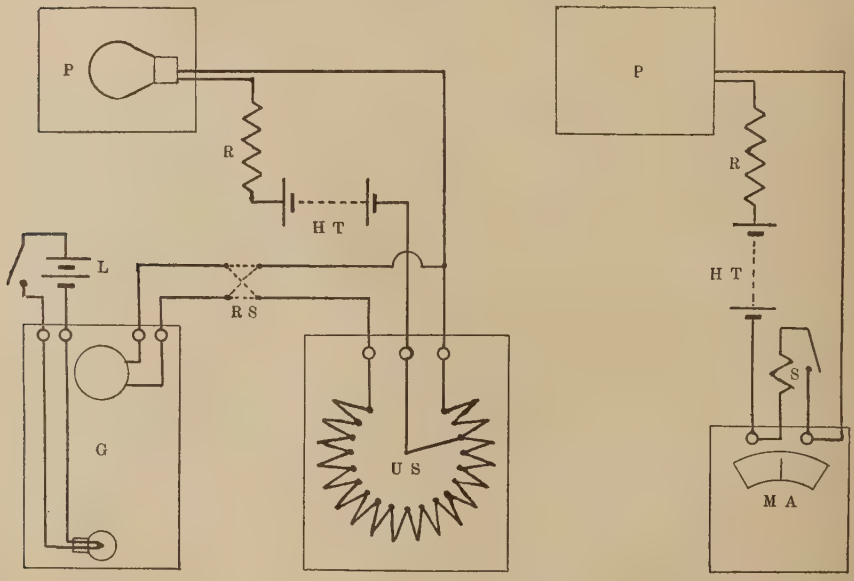

Fig. 1.

Arrangement of photometers and galvanometers at shaded base, left, and open base, right. L, galvanometer lamp battery. G, portable mirror galvanometer. RS, reversing switch. US, universal shunt. HT, high tension batteries, 60 volts. R, safety resistances, 10,000 ohms. P, photometers, the photo-electric cell is indicated in that on the left. MA, Onwood micro-ammeter. S, shunt, to one-fifth. For standardisation of G, the P circuit was removed, and MA, with dry cell, connected to US instead. For comparison of the three photometers they were connected, in quick succession, to US, but only one is shown in figure.

readings must be multiplied in order to find the vertical illumination, also to an accompanying paper (1929) on uranyl oxalate photometry.

It may be said, however, as an indication of the relative unimportance of this correction, that when the altitude of the light is 50°, the factor is 1·01, *i.e.*, the correction is only 1 per cent., and with the light uniformly diffused from the whole sky, the factor is only 1·06, the same figure applying to a beam of direct sunlight of altitude 30°.

Method of Measuring the Photo-electric Current.

In fig. 1, the arrangement of the photometers and galvanometers is shown, as used in 1928. We have lately acquired, however, an Onwood micro-ammeter (Type No. 3140) which reads directly to 0·1 μa, or by estimation to 0·02 μa. This is a more convenient instrument than the Tinsley portable galvanometer, and appears to be sensitive enough to measure the light in all but the most heavily shaded situations. In the 1927 work the arrangement was that both photometers were used alternately, connected with the Tinsley galvanometer, without the interposition of the universal shunt; the latter, which is of the Ayrton-Mather type, was found necessary, using the more sensitive Burt cells. Table I shows the constants of the galvanometers employed.

Table 1.

Portable galvanometers used in making photo-electric measurements in the field.

Galvanometer.	Description.	Res., ohms.	Scale div. per μa.	Length of Scale.
Onwood No. 3,100.	Pointer micro-ammeter.	224	2	15 × 2 μa.
Onwood No. 3,140.	Do., side zero.	312	10	12 μa.
Tinsley Portable.	Lamp and scale in box.	337	25·0*	50 × 2 mm.
Onwood No. 3,063.	Lamp and scale, specially fitted at 1 m., in box.	700	1,000*	250 × 2 mm.

Photo-electric Cells.

Photometer H contains a potassium vacuum cell, with a maximum sensitivity near 4,000 Å.U., as shown in fig. 2 of our 1928 paper. The cell was re-mounted, as ground glass was not found to be a sufficiently good diffusing substance. It is now carried on the under side of the ebonite lid of a light-tight box, the pupil of the cell occupying a hole in the lid 1·4 cm. in diameter; the outer edge of this hole is steeply chamfered off to admit low angle light. The aperture is covered by a diffusing glass window, cemented to the outside of the lid. The glass is opal-flashed on each surface, and is quite the best diffusing substance

* On reversal.

we have found as yet. It reduces the diffused light reaching the cell only by about one half, and the effect on the colour sensitivity curve is small. The cell was, at first, mounted with a guard wire, but this we found unnecessary for our work. Standardization was carried out against an open carbon arc lamp; this was chosen, since of those artificial sources which are readily reproducible at any time, it most nearly resembles daylight in its spectral energy distribution.

As, however, the maximum sensitivity of the eye is in the yellow-green, whereas that of the cell is in the violet, daylight, which is considerably bluer than arc light, is appreciably brighter on the photo-electric scale than it is by visual comparison. This, however, is one of the fundamental difficulties inherent in photometry of different light sources. It, of course, does not affect the value of the daylight factor. It was found that photometer H gave 10^{9} amp. per 40 metre candles, at 60 volts anode potential. For small changes in voltage, a correction is applied by deducting 0·1 m.c. for every volt above 60, or by adding 0·1 m.c. for every volt below 60. This holds fairly well for voltages from 50 to 85, but it is preferable to keep between 60 and 70. In practice it has been kept between 57 and 63 volts. The correction for the variation of reflection loss with obliquity was found to be very close to the theoretical value shown on page 280 of our 1926 paper. For angles of incidence of pure sunlight from 90° to 50° the factor lies between 1·00 and 1·01. At 40° it is 1·02, at 30° 1·06, and at 20° 1·16. The value for diffused light is 1·06, the same as for pure sunlight at 30°. This cell and that of photometer G were obtained from the General Electric Company. Tests were carried out on G, also on L, a similar cell mounted in a submarine photometer, and no change in sensitivity could be detected over a period of 8 months, using a small test lamp run at constant voltage as described by us previously. The lamp was reserved for the purpose.

The standardization of photometer H was based upon the work of Forrest (1913) and Allen (1921). The former has shown that the luminosity perpendicular to the face of the positive carbon is about 173 candle-power per sq. mm., and the latter found that, under the conditions of his work, the current was 0·746 ampere per sq. mm. Combining these two we get 232 c.p. per ampere in a direction perpendicular to the face of the positive carbon.

The carbons (7 mm. solid) were vertical, the positive being above, and a magnified image of the arc was thrown on a screen by means of a lens. This enabled us to ensure (*a*) that the end of the positive carbon was maintained in the same position, (*b*) that the end was very nearly horizontal, and (*c*) that the arc was sufficiently long to ensure that, at an angle of 45° to the vertical, no part of the positive carbon was blocked out by the negative one. The photometer to be tested was fixed at a measured distance (15 to 20 cm.) from the positive crater, the line joining the crater and the centre of the pupil making an angle of 45° with the vertical and being perpendicular to the window of the photometer. The candle-power of the arc along this line was obviously $0{\cdot}707 \times 232$ times the current in amperes. Thus, by measuring this current with a good ammeter, when the conditions were steady, the illumination on the

photometer was found. About eight to ten readings of the photo-electric current were taken, the extreme readings deviating about 5 per cent. from the mean.

In this way it was found that, as already mentioned, photometer H gave 10^{-9} amp. per 40 metre candles.

Photometer H was only used in our 1928 work to calibrate two other photometers, B 188 and B 223, which were selected for use in the open and in shaded situations, respectively.

The B photometers contain sodium vacuum cells obtained from Dr. R. C. Burt, of Pasadena. They resemble electric lamp bulbs, and are mounted on standard radio valve sockets with bayonet joints. The metal has been deposited by electrolysis of the glass, and the perfection of the sodium layer thus obtained renders them very sensitive, so that one can obtain a sensitivity equal to or greater than that obtainable by using a gas-filled cell, which, as is well known, is inconstant, and requires very frequent calibrations. The colour sensitivity of the sodium cell is shown by Burt as having a maximum at about 3,600 Å.U. The two B photometers were constructed with opalised glass tops 26·5 × 21·5 cm. so as to take full advantage of the wide angle illumination of the cell. No guard wire was used. They were standardised against H, the currents being measured by the portable galvanometer and shunt (see fig. 1).

The photometers were placed side by side in the open, commencing at 11.15 G.M.T., on September 17th, with a grey sky and east wind, the sun being scarcely visible through cloud. The light conditions were thus tolerably stable, and readings were made with H, B 223 and B 188 in quick succession. In all, five readings were made with H, and four with each of the others. From the averages of these, it appeared that B 188 was 19·4 times, and B 223 50·3 times as sensitive as H, so that 10^{-9} amp. corresponds to 2·06 m.c. with B 188 and to 0·795 m.c. with B 223. These figures are for an anode potential of 60 volts. Corrections for alterations in sensitivity were obtained from data supplied by Dr. Burt. In the neighbourhood of 60 volts, the correction amounts to 0·5 per cent. per volt for B 223, and 0·2 per cent. for B 188.

TABLE 2.

Vertical illumination measurable with various photometer and galvanometer combinations, using 60 volts anode potential.

Photometer.	M.c. per μa.	Galvanometer.	Limit of Reading. Current in μa.	Illumination in m.c.
H	40,000	Tinsley.	0·004	160
B 188	2,060	Onwood No. 3,100.	0·05	103
B 223	795	,, No. 3,140.	0·02	15·9
B 223	795	Tinsley.	0·004	3·2
B 223	795	Onwood No. 3,063.	0·0002	0·16

Table 2 shows the sensitivity obtainable by using the various photometers with the galvanometers listed in Table 1. The less sensitive Onwood micro-ammeter No. 3100 is best suited for use in the open, the current being shunted to 1/5 in bright sunlight. Onwood No. 3140 is more convenient than the Tinsley portable galvanometer, and sensitive enough for ordinary ecological work down to a daylight factor of about 0·1 per cent. One advantage is that no accumulator is required, and, of course, a pointer instrument can be read very rapidly. Onwood No. 3063 (Gambrell Bros.) has been included in the list for the sake of comparison of the sensitivities obtained, but it has not actually been tried as yet in the field.

Method of Observation.

Instead of using two separate galvanometers, the two photometers may be connected successively to the sensitive galvanometer and universal shunt, and alternate readings taken by a single observer, but at least one pair of long, well-insulated cables is required to connect the photometers in the open or the shaded site to the galvanometer for this purpose. Rubber-insulated high tension ignition cable, 8 mm. diameter, is used, any necessary joints being made by means of binding screws, mounted on paraffin wax blocks.

In the 1928 measurements cables 44 m. long were used to connect the photometer to the galvanometer, as shown on the left-hand side of fig. 1. The photometer was moved about to various positions while the measuring outfit remained in one spot. The measurements of full daylight were made, using the less sensitive photometer, B 188, and the micro-ammeter, the connecting cable being 4 metres long. The illumination at the open site was read at intervals of a minute or half-minute, the exact time being noted, while another observer made the measurements of illumination in the various shaded sites, and noted the time of each.

The area studied was the garden of the Old Vicarage at Antony, near Torpoint, in Cornwall. The open base selected was on the top of the garden wall, about 3 m. high, in a commanding position on the top of a hill, about the same level as the top of the tower of Antony Church, and well above the level of the roof of the Old Vicarage. The only obstructions to light are two rows of trees, one at some distance to the south-west, and the other rather nearer, but end on, to the east. Both these rows keep off a little low-angle light. Fig. 2 shows a plan of the garden and the various trees and flower beds, drawn approximately to scale.

The garden is situated on the north slope of a hill, below the wall base, to the south of which the ground is nearly level. It is all somewhat shaded, and some parts are heavily shaded. The behaviour of the plants in it has been noted for some years past, and the measurements recorded in this paper afford data for further observation on plant growth.

Illumination in Shaded Situations.

Reference may be made to the paragraph with a similar heading in our previous paper (1926). In that, it was pointed out that the daylight factor, δ, was more important throughout the year than the total light factor. The daylight factor is defined as the percentage of the vertical illumination, from a

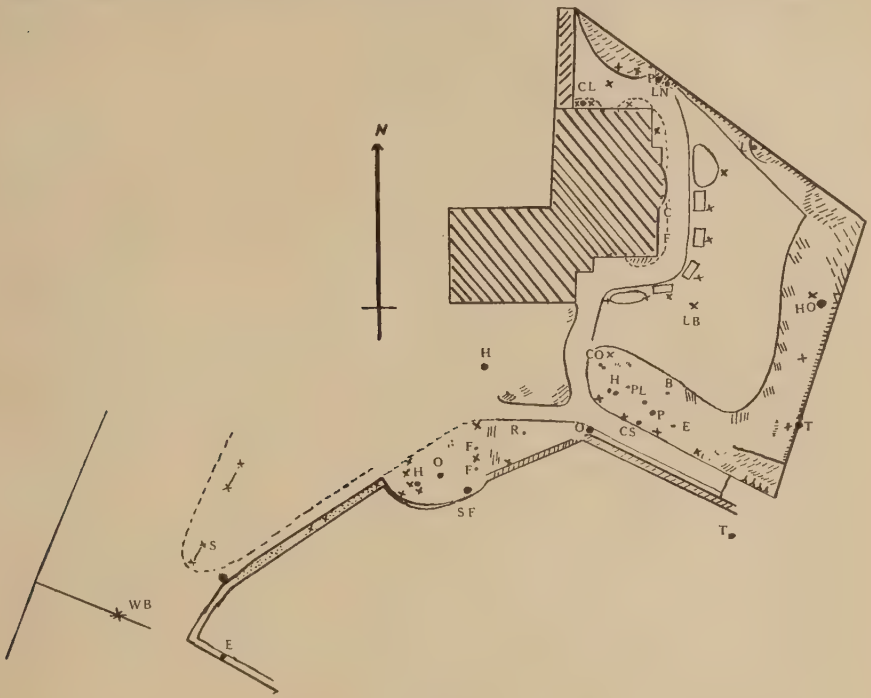

Fig. 2.

Plan of garden of Old Vicarage, Antony, approximately to scale. Positions of trees denoted by large dots; sites where observations made denoted by crosses. WB, standard open base, on wall; LB, partly shaded sub-base, on lawn. E, at south-west, *Ulmus campestris.* S, *Lathyrus odoratus.* H, *Ilex acutifolius.* O, *Quercus robur.* SF, *Abies pectinata.* F, *Fuchsia riccartoni.* R, *Rosa.* T, *Taxus baccata.* HO, *Quercus ilex.* E, *Eucalyptus globulus.* P, *Pinus sylvestris.* PL, *Prunus lusitanicus.* B, *Berberis vulgaris.* CS, *Cytisus scoparius,* var. *andreanum.* CO, *Crataegus oxyacantha.* C, *Camellia japonica.* L, *Larix europaeus.* LN, *Laurus nobilis.* CL, *Cytisus laburnum.*

sunless sky, which is received at the point in question. If the sky were always uniformly illuminated this would be a constant. In practice, however, want of uniformity and reflection from bright clouds may cause appreciable variations, even in the absence of direct sunlight.

When the sun is shining it directly affects the photometer in the open, but its effect at the shaded site is small (see Table 5 of our 1926 paper), as most of the apertures, through which the light reaches this site, do not admit direct

sunlight. Accordingly, when the sun is shining, we must eliminate the effect of direct sunlight on the photometer in the open, either by screening it off by means of a small object held at some distance from the photometer, or by dividing the reading of the unscreened photometer by the ratio, β, of the unscreened reading to the screened reading. This is more convenient, as the determination of the screened reading requires two observers, and the determinations of β need only be made at intervals.

Thus $\delta = \frac{V_s}{V_0}\beta$, where V_0 and V_s denote the vertical illuminations in the open and shaded sites, respectively.

TABLE 3.

To show degree of constancy of δ at sub-base on lawn, L.B. in fig. 2. Vacuum sodium cell. 13/10/'28.

G.M.T.	LIGHT.	V_0	V_s	$\frac{V_s\beta}{V_0} = \delta$.
1.15 P.M.	Sunny, $\beta = 1{\cdot}92$, $V_s/V_0 = 28{\cdot}8$ per cent.	54,500	15,700	55·8
2.19 ,,	Fairly uniformly overcast, $\beta = 1$.	16,300	9,140	56·0
2.20 ,,		15,700	8,950	57·0
2.21 ,,	Blue patches of sky near zenith from this onwards.	15,700	9,630	61·4
2.22 ,,	Broken cloud round sun, disc never visible.	16,800	10,300	61·4
2.24 ,,		17,900	11,000	61·4
2.25 ,,		19,200	13,000	67·7
2.26 ,,		20,700	13,700	66·2
2.34 ,,		24,000	15,300	63·7
	(Decomposition of Uranyl Oxalate. 30/5/'28.)			
5.40–8.40 A.M.	Overcast morning, calm, rain drops.	—	—	57·8
8.40–11.40 ,,	Very murky, visibility 2 miles, heavy shower, a little blue sky in N.W.	—	—	61·4
	(Gas-filled Cæsium Cell. 15/10/'27.)			
10.20 ,,	Clear sky, sun unclouded.	—	—	68

Table 3 shows that the value of δ does not, in fact, remain quite constant. The measurements indicate, however, that δ is of sufficient constancy to constitute a good index of the illumination at any site. Table 3 contains some values obtained using a photo-chemical method, namely, the decomposition of oxalic acid in the presence of uranium sulphate. This is described and discussed in an accompanying paper (1929), and it appears to agree well with the photo-

electric method. One value is also given in the table from measurements made using the caesium cell, and this accords tolerably well with the others. The rather higher value may be due to the relatively great sensitivity of this cell to green light, of which a considerable amount must have been reflected from the trees surrounding the site. Trees reflect but little blue light, and consequently the sodium photometer may be expected to give rather lower values than does the caesium.

The Plants and Light Intensities in the Garden.

Table 4 records the actual illuminations and values of δ obtained for a bed along which a row of geraniums (*Pelargonium zonale*) had been planted in 1927 in such a position that the middle portion was heavily shaded. When planted out all bore flower buds, and these naturally opened later on. The plant, however, which was in the deepest shade did not produce any further blossoms, and the plant to the west of it in somewhat less intense shade became lanky and flowered but poorly. Unfortunately, when the measurements were made on October 13th, the leaves had fallen from the Cytisus which shaded these two plants, but a determination on May 30th, using the uranyl oxalate photometer, gave 6·4 per cent. for δ. The shade in the rest of the bed, due to yew, a laurel hedge, Scots pine, and oak—as shown in the plan (fig. 2)—did not seem to have altered much since the summer.

Table 4.

Illumination at sites from east to west along bed to N. of path to Antony Church. Photometer on ground. Sites marked by × on plan. October 13th, 1928. Somewhat hazy blue sky; a few clouds.

G. M. T.	Site and Vegetation.	β	V_0 m.c.	V_s m.c.	δ
12.47 p.m.	Near Pelargonium A, flowered, rather lanky. *Ranunculus ficaria* abundant at all sites in this bed in spring.	1·73	49,000	5,000	17·6
12.48 „	Near Pelargonium B, flowered, rather lanky.	—	49,000	4,830	17·0
12.51 „	Further along, near site of Pelargonium C.	1·92	54,500	5,140	18·0
12.54 „	Under *Cytisus scoparius*, var. *andreanus*, branches bare. *Omphalodes verna* naturalized near here.	1·90	53,400	3,385	12·2
12.56 „	Under Cytisus, site of Pelargonium D in 1927.	1·92	54,500	3,390	12·0
12.58 „	E. of Pelargonium F, flowered, rather lanky.	1·90	53,400	3,870	13·9
1.0 „	S. of Pelargonium G, flowered well.	1·92	54,500	3,970	13·9
1.2 „	S. of Pelargonium H at west end, flowered well.	1·65	46,800	4,940	17·5
1.4 „	In sun, west of rhododendron bush.	1·90	53,400	30,500	—
1.6 „	Do., sun obscured.	1·00	38,100	10,700	28·3

Most gardeners have been troubled with the difficulty of selecting plants which will flower well in north aspects. This trouble has been experienced in situations on the north side of the Old Vicarage. The illuminations are shown in Table 5. The beds on the north wall, the position of which may be seen on the plan, are suitable for primroses and *Helleborus niger,* the values of δ being about 13 per cent. to 18 per cent. The garden nasturtium, *Tropaeolum major,* when sown in these beds, grows very poorly, the plants being lanky and etiolated. They die without flowering.

TABLE 5.

Illumination at sites on north side of house. November 2nd, 1928. North wind, with some large white clouds, sun clear. β taken as 2·2, throughout, from one set of measurements.

G. M. T.	SITE AND VEGETATION.	V_0	V_s	δ
11.54 A.M.	Corner next porch, *Primula veris* thrives, also *Veronica hederæfolia.*	43,100	2,490	12·8
11.56 ,,	Do., sloped N.	41,500	2,550	13·6*
11.58 ,,	5 ft. out, *Helleborus niger* thrives, *V. Hederæfolia* more abundant, a few plants of *R. ficaria.*	40,900	3,380	18·3
12.0 ,,	Do., sloped N.	40,900	3,350	18·0*
12.2 P.M.	Bed E. of window.	41,500	2,940	15·6
12.4 ,,	Do., sloped N.	38,200	3,740	21·6*
12.6 ,,	Middle of path, opposite window.	45,300	5,530	26·8
12.8 ,,	Under bushes, no growth.	46,900	854	4·0
12.12 ,,	2 ft. further out, on ivy, sloped S.	41,500	902	4·8*
12.14 ,,	Under bushes, where *Convallaria majalis* thrives.	38,200	1,180	8·6
12.15 ,,	Do., sloped S.	29,400	1,620	12·1*

In the bed to the east of the window, *Alyssum maritimum* grew moderately, but failed to produce flowers. The site is shaded, not only by the house, but by evergreens about 15 feet high, across the path as shown in the plan, and at the other side of the road there are tall elms. From east to west the evergreens are *Ilex acutifolius, Laurus tinus, Euonymus japonicus, Berberis darwinii,* and *Choisya ternata.* In the thickest shade under these bushes, nothing grows. The daylight factor was 4 per cent. on a barren spot near the edge, so probably the dryness of the situation has something to do with this phenomenon. A little further along, towards the east, *Convallaria majalis* thrives, with δ 8·6 and rising to 12·1, on the south aspect. Beds of the plant which have been left undisturbed from year to year, are usually infested with weeds, but in this case singularly few appear, owing, no doubt, to the combination of considerable shade and lack of moisture.

* Value with sloped photometer really δ_M, but printed under δ for convenience.

TABLE 6.

Illumination at sites on east and south sides of house. November 2nd, 1928. North wind, with some large white clouds, dry. Sun clear or temporarily obscured. Cloudy and dull after 2 p.m.

G. M. T.	SITE AND VEGETATION.	β	V_0	V_s	δ
	Sites on lawn.				
12.18 P.M.	On E. of large north bed.	1·0	10,200	4,860	47·6
12.20 ,,	On E. of next bed.	1·0	9,600	6,230	64·9
12.23 ,,	On E. of third bed, opposite Fuchsia.	1·0	9,370	6,090	65·0
12.25 ,,	On E. of bed near S.E. corner of house.	1·0	11,340	8,750	77·1
12.40 ,,	On S. of smaller south bed.	2·2	41,500	14,200	75·5
12.42 ,,	On E. end of large south bed.	2·2	41,500	11,100	59·0
12.46 ,,	On W. end of do., sun on photometer.	—	34,900	20,400	[58·5]
	Sites close to wall.				
12.28 ,,	Under climbing rose near N. end of E. wall, north sky clear blue.	1·0	14,800	2,290	15·5
12.32 ,,	Under Camellia sp., C on plan, near E. wall.	2·2	41,500	634	3·3
12.36 ,,	Under Fuchsia sp., close to young Taxus, near E. wall.	2·2	42,000	887	4·8
	Sites on east of lawn.				
2.21 ,,	Under very large *Quercus ilex* where *Hypericum calycinum* thrives, on east of lawn.	1·0	11,500	826	7·2
2.27 ,,	Between Quercus and large Taxus, by young Taxus.	1·0	9,370	1,230	13·1
2.32 ,,	Under large Taxus, sloped N.W.	1·0	6,550	235	3·6*
2.36 ,,	Do. horizontal.	1·0	6,750	211	3·1

Table 6 records the illumination in the garden beds round the house, and it may be seen that the north-east corner is considerably shaded, both by the house, and by large specimens of *Pinus sylvestris* and *Laurus nobilis*. The south-east corner is the best lighted. These situations with daylight factor between 60 per cent. and 80 per cent. would ordinarily be considered fairly open. In rather heavy shade under a large Camellia bush δ was reduced to 3·3 per cent. Under this young plants of *Ilex acutifolius* sprang up, and a species of white anemone appears each spring under an adjoining fuchsia bush. Young self-sown *Taxus baccata* thrive.

It is noticeable that at the east of the lawn, a very large holm-oak (*Quercus*

* Value with sloped photometer really δ_M, but printed under δ for convenience.

ilex) only reduces the value of δ to 7·2 per cent., but a fine specimen of *Taxus baccata,* aided by evergreens, lowers δ to 3·1.

From the hill on which the wall base is situated, a path bounded on the south-east by an earth bank about four feet high runs down in a north-easterly direction. The bank is topped by a hedge of deciduous saplings, which had run wild and attained a height of 15 or 20 feet in places. The illumination at sites along this bank was (Table 7), in consequence, reduced to about 20 per cent., or with the photometer sloped to the north-west, about 30 per cent. Quite in keeping with the results found in Cawsand woods in 1925, this was a suitable habitat for mixed grasses, with *Urtica dioica,* and *Bromus asper,* a grass characteristic of shaded sites.

TABLE 7.

Illumination at sites on bank, facing N.W., on steep hill leading to wall base, also under Ilex, Fuchsia, and Aucuba lower down as shown on plan. Bank and Ilex, 3rd November, 1928, dull and raining. Fuchsia, etc., 2nd November, 1928, dull. $\beta = 1$ throughout.

G. M. T.	SITE AND VEGETATION.	V_0	V_s	δ
11.13 A.M.	Midway along bank, Mixed grasses, *U. dioica*, *Bromus asper*.	15,600	3,380	21·6
11.16 „	Do., sloped N.W.	15,900	4,910	30·9*
11.20 „	Further down bank.	16,800	3,130	18·6
11.22 „	Do., sloped N.W.	17,000	5,280	31·0*
11.25 „	N. end of bank.	15,900	2,930	18·4
11.27 „	Do., sloped N.W.	15,500	4,440	28·6*
11.30 „	Under outer edge of Ilex, *Urtica dioica* thrives.	14,400	4,790	33·2
11.33 „	Do., sloped W.	12,400	5,430	43·8*
11.35 „	Half way in towards Ilex trunk.	11,500	818	7·1
11.38 „	Do., sloped W.	11,100	1,960	17·7*
11.44 „	Near trunk.	10,800	136	1·3
11.48 „	On bank, near trunk by *Scolopendrium vulgare*, sloped N.	12,500	277	2·2*
11.50 „	On inner side of trunk on dead leaves, a little straggling Hedera.	12,500	157	1·3
	On 2/11/'28.			
2.50 P.M.	Under *Fuchsia riccartoni*, only Hedera, sloped N.N.E.	9,820	773	7·9*
2.53 „	Do., horizontal.	10,200	614	6·0
2.59 „	Further out, near box edge.	9,820	1,860	18·9
3.3 „	Under Aucuba, dry leaves only on ground, no Hedera.	9,710	136	1·4

* Values with sloped photometer are really δ_M, but are tabulated under δ for convenience.

Further down, under a large tree, *Ilex acutifolius*, the value of δ was reduced to 1·3 per cent. On the bank near it, several plants of *Scolopendrium vulgare* flourished on the north slope, the value of δ here being 2·2. It may be remarked that in the Cawsand area No. 1, site D, *S. vulgare* was found with δ as low as 1·9, a degree of shade which but few plants seem able to tolerate. As in Cawsand wood, *Hedera helix* straggles in the deep shade. The values of δ under the fuchsia, as shown in Tables 6 and 7, would doubtless have been appreciably lower, had the determinations been made before the leaves had begun to fall.

Table 8.

October 10th, 1927, 2.10 to 3 p.m. Photometer H on wall base. Photometer C, which is sensitive to green, used in the shade, with anode potential 94 volts. It was considered that the calibration of C against H, carried out at noon, was not sufficiently recent. Absolute values have accordingly been omitted as unreliable. The reading for the most heavily shaded site has been taken as unity, and the last column gives the ratios of this value to those for the other sites; corrections were applied for any changes in external illumination. Photometer at 60° to horizontal, when not horizontal.

	Relative illumination.
Sites to N. and N.W. of high hedge of evergreens, with shade from Q. robur. *See F.F. on plan.*	
Under Fuchsia, *Hedera helix* dominant.	1·00
Under Fuchsia, sloped N.N.E.	1·95*
Under Fuchsia, a little further out, *H. helix* dominant, one *Primula veris*, a few plants of *Circaea lutetiana*, sloped N.N.E. towards only aperture.	2·10*
Near border of bed, *C. lutetiana* dominant, little *H. helix*.	4·35
Site S.E. of last one, under 3 m. hedge of *Aucuba japonica*, *H. helix* dominant, no Circaea, sloped N.E.	1·23*
Further out, *H. helix* and *C. lutetiana*, sloped N.W., best opening.	3·12*
Outer edge of zone in which *C. lutetiana* was dominant, sloped N.N.E.	6·04*
Do. do. do. N.	6·12*
Do. do. do. N.W.	6·40*

* The values for sloped photometer are approximations to *M*, and are marked thus to distinguish them from values of *V*, with which they are usually tabulated for convenience.

TABLE 9.

Daylight factors determined by exposing uranyl oxalate in quartz tubes on May 30th, 1928. Overcast, then murky and heavy rain, no sun, but sun near emergence towards end. From 5.40 to 8.40 a.m., rate 2·05 c.c. per hour; 8.40 to 11.40, rate 2·63 c.c. per hour on wall base.

Period.	——	δ
5.40 8.40 A.M.	Lawn sub-base, δ = 56–57 by sodium photometer, overcast sky.	57·8
8.40–11.40 ,,	,, ,, δ 61·4–67·7 by photometer, broken sky.	61·4
5.40–8.40 ,,	On site where *Lathyrus odoratus* failed in 1927.	60·7
5.40–11.40 ,,	By Pelargonium A of Table 4, where δ = 17·6 by photometer.	18·6
5.40–11.40 ,,	By Pelargonium D of Table 4, where δ = 12·0 by photometer, with leaves down.	6·4

In Table 8 some of the 1927 results are shown to illustrate the gradual decrease in *H. helix*, and the increase in *Circaea lutetiana*, as the illumination increased sixfold. In Table 9 are recorded a few values of δ obtained by the uranyl oxalate method, which is described in detail in an accompanying publication; it appears to be reliable, and to agree well with the photo-electric determinations.

It is suggested that the possible cause of the failure of a row of sweet peas (*Lathyrus odoratus*), where the value of δ was 60·7, is that this value is insufficient for their growth, especially as the site was on the north slope, and was shaded by the tall hedge previously mentioned, so that it only received direct sun after twelve o'clock. Before the hedge had grown so high, these plants had been grown successfully, in the same position. The hedge has now been cut, and further seeds sown.

The results in so far as they are recorded in the Tables give an idea of what can be done, but observation of the sites from year to year brings out the correlation between the degrees of shade and plant growth more closely than is possible in anything but a description in great detail.

We desire to acknowledge with thanks the receipt of a further payment from the Government Grant Committee of the Royal Society, which rendered possible the purchase of the photo-electric cells. We are also indebted to the Royal Dublin Society and the Marine Biological Association of the United Kingdom for general laboratory facilities in connection with the standardization of photometers and arrangement of apparatus.

Summary.

1. By the use of portable galvanometers, appropriate shunts, and large sodium vacuum photo-electric cells of the Burt type (which are only sensitive to blue, violet, and ultra-violet light), it is possible to measure the illumination in the open and in shaded situations simultaneously. Less satisfactory results

were obtained with a smaller vacuum potassium cell for work in the open combined with a gas-filled green-sensitive caesium cell for work in the shade. The apparatus with the Burt cells is portable and the large current yielded permits of the use of a robust Onwood type of micro-ammeter.

2. The adoption of double surface flashed opalised glass as a diffusing window for the photometers obviates the necessity of large obliquity corrections, which moreover, are different for each azimuth.

3. The results obtained for measurements of the daylight factor agree well with those determined by the rate of decomposition of uranyl oxalate solutions in quartz tubes.

4. The daylight factor is not a constant, but varies somewhat according to the distribution of the illumination in the absence of sunlight. Sunlight, too, may raise the value in certain cases. The factor is, however, sufficiently constant to be a useful index of the light received at any spot.

5. Data are presented showing the behaviour of certain plants growing in varying degrees of shade.

In the deepest shade measured, daylight factor, δ, 1·3 per cent., only straggling branches of *Hedera helix* were found. Further out *H. helix* is dominant, and with a six-fold increase in δ may give way to *Circaea lutetiana*. *Convallaria majalis* thrives with δ 8·6 rising to 12·1 with sloped photometer. Other examples are recorded, and the light distribution in a garden has been mapped out.

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No. 25.

A STUDY OF FUNGI FOUND IN MILK.

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(Plates 17 and 18.)

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A survey extending over the first five months of 1929 was made of fungi found in samples of milk examined in the course of a clean milk competition, carried out by the Departments of Dairy Bacteriology and Dairy Farming, University College, Cork.

The milk was plated on Nutrient Lactose Agar, to which sufficient Lactic Acid had been added to give the media a *pH* of 3·5, in order to prevent bacterial growth. The plates were then incubated at 70° F. for a week before examination. It was found that fungi frequently appeared in making cultures from milk, and it seemed desirable that these should be investigated in detail.

This was done in conjunction with the Department of Botany, University College, Cork.

Where inoculation experiments for pure cultures were made on uncooked root-vegetables, the latter were cleansed in distilled water, thoroughly sprayed in a 1/1000 solution of perchloride of mercury, and again rinsed in distilled water. Every precaution was taken to keep the vegetables and utensils free from contamination. The three species most frequently found, occurring in almost all the cultures, were *Oidium lactis*, *Acrostalagmus cinnabarinus*, and *Phoma* spp.

(1) *Oidium* (*Oospora*) *lactis*, Fresen (fig. 1, Pl. 17).—In cultures from milk, it appears as a creamy, white, circular flat growth, with concentric zones. No aerial hyphae, or a few very short moniliform hyphae, are sent up. The mycelium is septate and continuous at first, soon breaking into individual cells. Older growths show a torula-like condition at the edges of the cultures.

Grows on turnip, parsnip, and beet when kept in the dark. The vegetable first gets a dry wrinkled appearance, later a white mycelium appears, and finally rapid deterioration takes place, with pulping of the tissues and evolution of foul-smelling gases. When exposed to the light the erect white mycelium disappears, and the fungus changes to a torula condition, the vegetables becoming a slimy mass. It clots litmus milk thickly in 48 hours, with production of acid and decolourisation of litmus.

(2) *Acrostalagmus cinnabarinus* Corda (*Verticillium cinnabarinum* Reink & Berthold) (fig. 2, Pl. 17).—Frequently appears in cultures as a white, tufty mycelium, later changing to brick-red on all media. The fungus spreads, covering other growths without injuring them. The sterile mycelium closely resembles the mycelium of Phoma before the appearance of fructifications, having a twisted, rather withered appearance. The conidia are held together by mucus, forming a head which, when young, has the white glistening appearance of water droplets, but becomes a brownish-red when mature. Fig. 2A shows appearance under low power. Fig. 2B shows conidial heads under high power. Grows feebly on a wound in beet, also feebly on carrot. When cultured in litmus milk, the appearance of the milk is not perceptibly altered after 48 hours.

(3) *Sporotrichum carnis* (fig. 3, Pl. 17; fig. 1, A and B, Pl. 18).—Found very commonly. First isolated 28/2/29. All specimens found had the characteristic form of two or three small concentric circles, "crusty" or crystalline in appearance, with small droplets, and growing on top of a yeast colony (fig. 1A, Pl. 18), varying from 3·12 mm. to 3·9 mm. in diameter. Cultures were made on the following media in Petri dishes, and kept in a cupboard at a temperature of about 62° F.:—

Medium.	After 7 days.	After 14 days.
Potato Agar	Small felt-like patches scattered over dish.	Sparse growth, scattered, older patches showing a reddish-brown discolouration on under-surface.
Dextrose Agar	Scattered patches, felt-like, no droplets, yellow underneath.	Rounded patches, velvety looking, showing rings of growth. Centres of patches slightly raised, and with reddish-brown discolouration on under-surface.
Bacto-Beef Agar (fig. 1B, Pl. 18).	Small felt-like patches, yellowish and concave on under-surface.	Good felt-like growth, colour turning to a creamy yellow, with bright yellow droplets on older patches. Patches ringed and joined by mycelium not bearing aerial branches. Centres of patches raised, and under-surfaces yellow, shading to orange-brown and concave.
5 % Lemco Agar	Single white felt-like patch, pale yellow on under-surface.	Poor, flat "crusty" (powdery) growth, very flat, with a few scattered droplets, and slightly discoloured on under-surface to a reddish-brown.

Medium.	After 7 days.	After 14 days.
2 % Lemco Agar (fig. 3, Pl. 17).	Very sparse scattered growth, large clear droplets.	Not much advance in growth, very sparse, no discolouration on under-surface.
Krainsky's Dextrose Agar ...	Rather small patches, "crusty," with water droplets, under-surface yellow to orange at centre.	Yellow droplets, and general resemblance to the culture on Bacto-beef.
Czapek's Agar	One small white patch, more "fluffy" than any of the other cultures (*i.e.*, had more aerial hyphae), under-surface yellow.	One solid-looking, wrinkled patch, about the size of a halfpenny, velvety in appearance, no water droplets, creamy colour, with a thin white margin. Underside showed discolouration from pale yellow to reddish-brown.

When cultured in litmus milk, after 14 days there was a thin papery growth, and colour of the litmus was not changed; there was a green colouration on the underside of the fungus. After 27 days the litmus became amber-coloured, a slight purple discolouration remaining on top. This culture was verified by Mr. Brooks, who found it as a common mould on meat in cold storage, and described it in detail in the Trans. Brit. Mycol. Soc., viii, 3, p. 131, and text, fig. 4, 1923. This form is considered as allied to the species Aleurisma Link, as understood by Veullemin (*fide* E. W. Mason).

(4) *Hormodendrum* (fig. 4, Pl. 17).—Of very frequent occurrence. Cultures were made on the same media as Sporotrichum, and examined after 14 days:—

Medium.	Appearance after 14 days.
Potato Agar	Small solid patch, $\frac{3}{4}'' \times \frac{1}{2}''$, felt-like, and olive-green in colour, lightening towards margin.
Dextrose Agar (fig. 4A) ...	Growth similar to that on Potato Agar, but surrounded by a lighter margin of sterile hyphae; conidia 3 or 4 in a chain; much secondary branching of conidia.
Bacto-beef Agar	Growth similar to that on Dextrose Agar.
5 % Lemco Agar	Very strong growth in small patches scattered over the dish, of a darker colour than the first three cultures. Spores not in chains.
2 % Lemco Agar (fig. 4B) ...	Scattered growth; very sparse, the mycelium appearing to grow deeper down into the medium than in the other cultures. Aerial hyphae not so dense as in other dishes, and are more fluffy-looking. Spores in chains of from 4 to 7, and closely resemble Hormodendrum elatum. (Fig. 4B, Pl. 17.)
Krainsky's Dextrose Agar ...	Resembled growth on Potato Agar.

This fungus showed a tendency to grow in water, forming a mycelium resembling Fumago in appearance. This form would not flourish in solid media. When inoculated in a wound in swede turnip and potato, a black discolouration appeared, and examination showed the presence of spores resembling those of Cladosporium, with some mycelium.

When cultured in litmus milk, a thick convoluted mass of the characteristic greenish-black colour was formed, filling half of the tube. Digestion of the milk took place with a little production of acid.

(5) *Trichothecium roseum* Link (fig. 5, Pl. 17; fig. 2, A and B, Pl. 18).—Occurs very frequently, and forms a powdery layer, varying in denseness according to the medium; at first white, later changing to pale pink. The mycelium is creeping, branched, and septate. The hyphae are white, the conidiophores upright, sparingly septate, mostly unbranched, and slightly swollen at the end. The conidia are terminal, formed one after another, but they remain hanging when full grown, forming a head. They are pear-shaped, two-celled, and very slightly constricted at the dividing wall. They are at first hyaline, then pale pink.

When cultivated in litmus milk, spore production is very dense, forming a firm layer on the surface, with the characteristic pink colouration. Digestion of the milk takes place with a slight acid reaction, and with a light-coloured deposit at the bottom of the tube.

(6) *Stysanus microsporus* Sacc. (fig. 6, Pl. 17).—Occurred on two occasions. The heads grow singly in groups, except when cultured on dextrose agar, when loosely panniculate branching was observed, as in fig. 6B, Pl. 18. When young the spores are black, but when old change to a glistening silver grey. Height of growth on Czapek's Agar = 1 m.m.; on 5 per cent. Lemco = ·5 m.m. When cultured in litmus milk, a very strong convoluted growth is observed. There is no production of conidial heads. It gives an acid reaction.

(7) *Mucor racemosus* Fres. (fig. 7, Pl. 17).—Mycelium creeping and dense, the colour varying from dirty yellow to white or grey. Sporangia terminal, on branched or unbranched sporangiophores, variable in size, and brownish-yellow. The sporangiophores are of variable length. The chlamydospores are characteristic, and present both in the mycelium and sporangiophores. They are globular or cask-shaped, and contain glistening spores. The columella is club-shaped. The capsule breaks away when mounted in lactic acid and cotton blue for examination, and leaves a collar round the columella. Clots litmus milk thickly within 48 hours, changing the blue to a pure white, with trace of red colour on the surface.

(8) *Mucor corymbifer* Cohn (*Absidia Lichtheimi* Ledner (fig. 8, Pl. 17).—Isolated on three occasions. It has a whitish-grey loosely matted form spreading over the other growths. The hyphae are long, bending down on coming in contact with the cover of the Petri dish.

The sporangia, though very minute, are visible to the naked eye as small dark specks. The sporangiophores bear a terminal sporangium, and lateral sporangiophores sometimes in the form of an umbel.

Largest sporangia 70μ in diameter — smallest, 10μ–20μ. They are dark brown, and apophyses are present which are at first light coloured, but turning dark with age. Structures in fig. 8A are numerous in the medium. They are

irregular in shape, and a greenish-brown colour, with granular contents. Projections from the main body of the mass grow up into colourless mycelia. We can find no reference to these bodies in the literature available; similar bodies occurred in *M. mucedo* (fig. 10, B and C). When cultured in litmus milk, it coagulated with production of acid, soft curd, and separation of whey.

(9) *Mucor mucedo* Linne (fig. 10, Pl. 17).—A very common form, with dirty white mycelium and dark heads. The branching mycelium in the medium gives off erect, unbranched sporangiophores. Sporangia = 70μ–140μ × 50μ–80μ. Spores, 6μ–12μ × 3μ–6μ. Similar structures to those figured in *Mucor corymbifer* (figs. 8A, 10, B and C) were found, which on transference to fresh medium gave out tubes, as in *M. corymbifer*, growing into the ordinary mycelium.

These chlamydospores (?) appeared again as the culture staled.

(10) *Mucor alternans* Van Tieghem (fig. 9, Pl. 17).—A dirty-yellow growth, low and creeping, not having the usual macroscopic appearance of a Mucor. Sporangia of various sizes were on short stalks, branching as in diagram. Spores = 2μ–3μ × 5μ–7μ. When grown in litmus milk, the curd is coagulated, and the litmus decolourised. There is a strong growth of the fungus on the surface with aerial hyphae 1″–1¼″ high.

(11) *Thamnidium elegans* Link (fig. 11, Pl. 17). — Considered entirely saprophytic. When first cultured it spread rapidly, and infected a dish, opened for examination, with a very strong growth. Young forms are difficult to distinguish from a Mucor until secondary sporangia appear. Spores = 8μ–10μ by 6μ–8μ; being the same size in the primary and secondary sporangia. Secondary sporangia generally fall off intact, and when grown in 2 per cent. sugar solution swelled to 7 or 8 times their original size without showing signs of bursting. When grown in litmus milk, coagulation of the curd with decolourisation of the litmus takes place. The curd is soft, with marked separation of whey, and film on surface.

(12) *Pilobolus crystallinus* was found on two occasions.

(13) *Botrytis cinerea* Pers. (fig. 12, Pl. 17; fig. 3, Pl. 18).—Occurred on three occasions as light greyish-brown tufts. When cultured it produced sclerotia and microconidia on the mycelium, as in fig. 12, Pl. 17. The hyphae are dark green, and the conidia, at first colourless, are later tinged with brown. Sterile hyphae were produced on the ends of the mycelia. It also grew well on potato sections, producing a similar result. Spores, 9μ–12μ × 6μ–10μ, from both kinds of conidia. When cultured on litmus milk, there was a growth on surface, and a bad odour was produced.

(14) *Aspergillus Spp.*—About three specimens of Aspergillus were fairly common; of these, one has been identified as belonging to the *glaucus* group (Thom). Ascospores are necessary for the further identification, and these have not yet appeared.

(15) *A. luteo niger* (Lutz) (fig. 13, A and B, Pl. 17; fig. 4, Pl. 18).—Appeared on one occasion; the mycelium at first white, then golden yellow, and

the heads pass through shades from pale yellow to dark brown. The spores when examined dry are seen to have colour bars and tubercules. These disappear when mounted in fluid, the conidia appearing smooth and globose. Primary and secondary sterigmata are present on spherical vesicular heads. Measurements are given on the diagram. The spores are globular, 5μ in diameter, hyaline when young, later fuscous. When grown in litmus milk, rapid digestion takes place, with strong production of acid. The growth of the fungus is very strong in a thick convoluted mass. This particular species of Aspergillus was recognised to be a rare species when found, and a culture was forwarded to Dr. C. Thom (Washington), who identified it as *A. luteo-niger*. The inference drawn from the appearance of cultures is to the effect that the spores are elastically projected, although the act has not yet been actually observed under the microscope.

(16) *Aspergillus terreus* Thom.—Of frequent occurrence, varying in colour from white to brown, passing through shades of pinkish cinnamon, according to age. Vesicle, 12–18μ, bearing sterigmata in two series, closely packed. Primary sterigmata = 2–2·5μ × 7–9μ. Secondary = 2–2·5 × 5–7μ. Conidia are slightly elliptical to globose, 2·2–2·5μ or 3μ.

This form is common in America, but has not been previously received by Thom from Europe.

(17) *Penicillium Spp.*—Several different species of Penicillium were found, but owing to the largeness of the group no steps have been taken to establish the identity of individual species.

(18) *Phoma Spp.* (fig. 5, Pl. 18).—Two species of Phoma were very common. One species was black, and the other pinkish-brown. A microscopic examination shows light-coloured hyphae with dark spots. These latter proved to be pycnidia, with one or two ostioles, by which the spores were extruded in coloured solution. Further investigations are being carried out on these species.

(19) *Torula Spp.* Pers (black) (fig. 16, Pl. 17).—Was found on one occasion.

(20) *Macrosporium sarcinula* Berk (fig. 14A, B, C, Pl. 17).—Found on one occasion. The hyphae are at first light-coloured, turning a brownish-black, septate, and spreading. The conidiophores are very short and swollen (fig. 15A). The conidia are constricted off in chains, a rare occurrence in this form, hyaline and smooth when young, dark and warted when older. They have a network appearance owing to formation of septa, and are constricted at the dividing walls. Spores very variable in size.

(21) *Stemphyllium botryosum* Wallr. (fig. 15A, B, C, Pl. 17).—Found on two occasions. Very similar to *Macrosporium sarcinula*, but the conidia are single, the conidiophores longer and thinner—may be branched or unbranched. The conidia are not so constricted as in *Macrosporium sarcinula*, and more warted.

Summary.

A survey extending over the first five months of 1929 was made of fungi found in samples of milk examined in the Department of Dairy Bacteriology, University College, Cork, in connection with a clean-milk competition. The following were found:—

(1) *Oidium* (*Oospora*) *lactis* Fresen
(2) *Acrostalagmus cinnabarinus* Corda
(3) *Sporotrichum carnis* Brooks and Hansford
(4) *Hormodendrum* Spp. Bonord
(5) *Trichothecium roseum* Link
(6) *Stysanus microsporus* Sacc.
(7) *Mucor racemosus* Fres.
(8) *Mucor corymbifer* Cohn
(9) *Mucor mucedo* Linne
(10) *Mucor alternans* Van Tieghem
(11) *Thamnidium elegans* Link
(12) *Pilobolus crystallinus* Tode
(13) *Botrytis cinerea* Pers.
(14) *Aspergillus* Spp.
A. glaucus group (Thom)
(15) *A. luteo-niger* (Lutz)
(16) *A. terreus* (Thom)
(17) *Penicillium* Spp.
(18) *Phoma* Spp.
(19) *Torula* Pers.
(20) *Macrosporium sarcinula* Berk
(21) *Stemphyllium botryosum* Wallr.

Many of these fungi had not been previously reported as having been found in milk. Their presence is probably accounted for by contamination of the milk due to the conditions under which the cows were housed, fed, and milked, and to improper cleansing of the dairy utensils.

Type cultures of these fungi have been deposited in the National Collection of Type Cultures, Lister Institute, Chelsea, London.

We desire to acknowledge with thanks the valuable assistance in identification and verification rendered by Dr. E. J. Butler, C.I.E., D.SC., F.R.S., M.B.; Mr. E. W. Mason, M.A., M.SC., and Mr. S. F. Ashby, B.SC., of the Imperial Bureau of Mycology, Kew Green, Surrey; Mr. F. T. Brooks, M.A., Cambridge; Dr. C. Thom, Microbiological Laboratory, Bureau of Chemistry, Department of Agriculture, U.S.A.; and to thank Professor C. Boyle, M.A., PH.D., Dean of the Faculty of Dairy Science, University College, Cork, for facilities afforded for carrying out the investigations.

Plate 17.

FIG.

1. *Oidium lactis* Fresen.
   A = ordinary mycelium with aerial hyphae.
   B = torula condition.
2. *Acrostalagmus cinnabarinus* Corda.
   A = low power, general view.
   B = conidial heads, high power.
3. *Sporotrichum carnis.*
   A = Sporangiophores under high power.
4. *Hormodendrum.*
   A = Form on dextrose agar.
   B = Form on 2 per cent. lemco agar.
5. *Trichothecium roseum* Link.
   A = single conidium budded off, a second being formed at X.
   B = Head of conidia.
6. *Stysanus microsporus.*
   A = solitary heads.
   B = branching evident on dextrose agar.
   C = single head enlarged.
   D = section through coreme, showing fibrous hyphae from which conidial chains spring.
7. *Mucor racemosus* Fres.
   A = Chlamydospores in mycelial hypha.
   B = aerial hyphae with sporangia and chlamydospores.
8. *Mucor corymbifer* Cohn.
   A = structure resembling chlamydospore in medium.
9. *Mucor alternans.*
10. *Mucor mucedo* Linne.
    10 B and 10 C = structures resembling 8A.
11. *Thamnidium elegans* Link.
    A = general structure, low power.
    B = secondary sporangia highly magnified.
12. *Botrytis cinerea* Pers.
    A = general appearance, low power.
    B = same magnified.
13. *Aspergillus luteo-niger* Lutz.
    A = section (transverse) through head, showing vesicle, sterigmata, and some chains of conidia.
    B = spores under high power.

FIG.

14. *Macrosporium sarcinula.*
    Showing condia in short chains, hyaline and smooth when young—later dark and warted.
    A = sporangiophore.

15. *Stemphyllium botryosum.*
    A = general appearance, high power.
    B, C, and D.—Conidia greatly magnified.

16. *Torula* Pers.
    General appearance, high power.

PLATE 18.

1. *Sporotrichum carnis.*
    A = microphotograph of colony 3·12 mm. in diameter.
    B = culture on bracto beef agar.

2. *Trichothecium carnis* Link.
    A = growth of colony on potato agar.
    B = growth of colony on bracto beef agar.

3. *Botrytis cinerea Pers.*
    Culture on potato agar, showing black sclerotia, and dark hyphae bearing conidia.

4. *Aspergillus luteo-niger* Lutz.
    Culture on dextrose agar.

5. *Phoma.*
    Culture on dextrose agar.

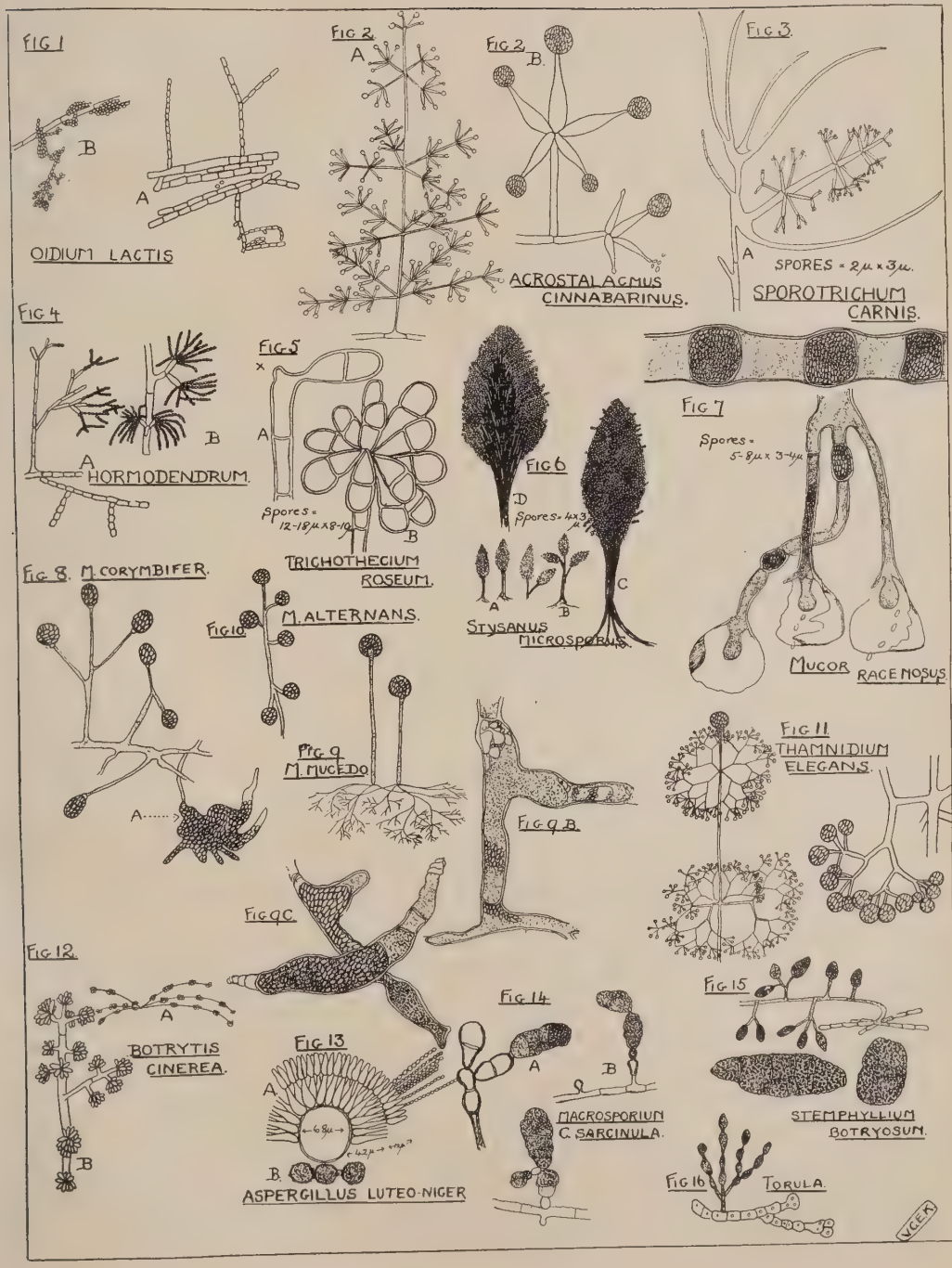
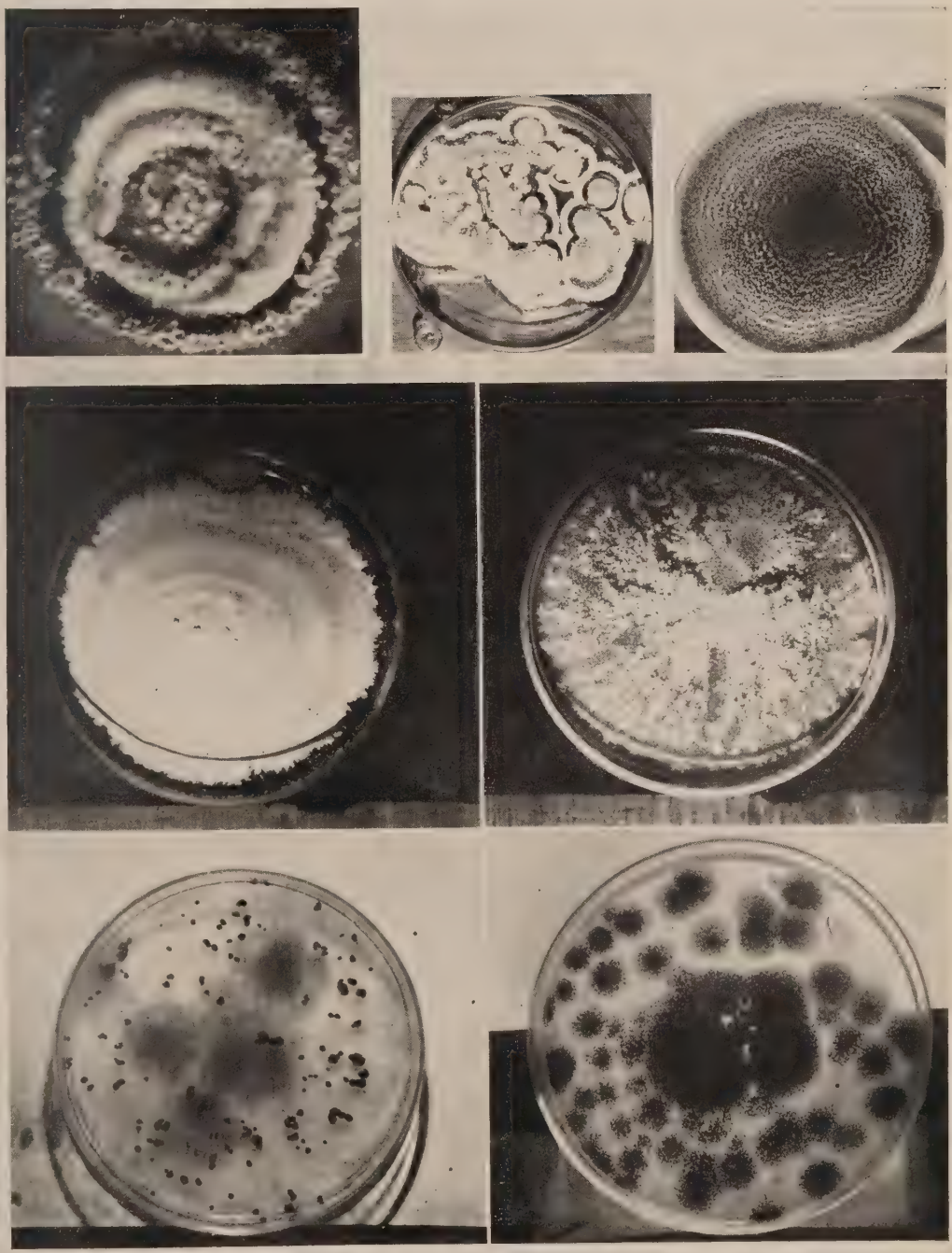


FIG 1
B
A
OIDIUM LACTIS
FIG 2.
A
FIG 3.
B.
ACROSTALAGMUS CINNABARINUS.
FIG 3.
A
SPORES = 2μ x 3μ.
SPOROTRICHUM CARNIS.
FIG 4
A
B
HORMODENDRUM.
FIG 5
X
A
Spores = 12-18μ x 8-10μ
B
TRICHOTHECIUM ROSEUM.
FIG 6
D
Spores = 4x3 μ
A
B
C
SYSANUS MICROSPORUS.
FIG 7
Spores = 5-8μ x 3-4μ
MUCOR RACEMOSUS
FIG 8. M. CORYMBIFER.
A
FIG 10
M. ALTERNANS.
FIG 9
M. MUCEDO
FIG 9 B
FIG 11
THAMNIDIUM ELEGANS.
FIG 9C.
FIG 12.
A
B
BOTRYTIS CINEREA.
FIG 13
A
B
ASPERGILLUS LUTEO-NIGER
FIG 14
A
B
MACROSPORIUM C. SARCINULA.
FIG 15
STEMPHYLLIUM BOTRYOSUM.
FIG 16
TORULA.
VGER



No. 26.

THE URANYL OXALATE METHOD OF DAYLIGHT PHOTOMETRY AND ITS PHOTO-ELECTRIC STANDARDIZATION.

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AND

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Introduction.

The action of light upon uranyl salts has been known since the work of Bucholz (1805), who observed that alcoholic solutions of both uranyl sulphate and nitrate were decomposed by light, the metal being precipitated as a complex hydroxide. Niepce de Saint-Victor and Corvisart (1859) appear to have been the first to record the photolysis of oxalic acid in presence of uranium salts.

Seekamp (1862) found that, whereas the decomposition of oxalic acid solutions in glass vessels was very slow when exposed to sunlight, yet, in presence of uranium salts, the decomposition was rapid, with the production of CO, CO_2, H_2O, and H.COOH. Substituting succinic acid for oxalic, he got propionic acid and CO_2.

Richardson (1894) noted the production of CO, CO_2 and H_2O_2 by the action of sunlight on oxalic acid, and Bacon (1907) showed that the production of H_2O_2 catalysed the reaction, so that the rate of disappearance of the acid was greater in the evening than at noon, whereas of course the light was diminishing. In the presence of uranyl sulphate no such production of hydrogen peroxide occurred, so that the rate of destruction was a measure of the light intensity. Richardson also observed that, when exposed to red light only, there was no decomposition of oxalic acid.

Bacon showed that the photocatalytic activity of uranium salts was not connected with their radioactivity; this was later confirmed by Berthelot and Gaudechon (1913) and by Landau (1913), who also found that chromium—he used the nitrate—has some photocatalytic power, and pointed out that it resembles uranium in belonging to Group 6 of the Periodic Table. Bacon (1910) concluded that fluorescein had no accelerating influence upon the photolysis of oxalic acid, and similar negative results were obtained by Berthelot and Gaudechon with other fluorescent substances.

Bacon considers the decomposition of oxalic acid in sunlight to be mainly $H_2C_2O_4 = CO_2 + CO + H_2O$, since the amount of formic acid produced is

small, and the quantity of uranyl salt reduced to uranous during the initial stages of the reaction is also negligible, so that for comparative measurements these factors may be disregarded. His analyses were carried out by titration with permanganate after removal of uranium salts with slight excess of ammonium hydroxide. The solutions were exposed in 100 c.c. Erlenmeyer flasks.

Bacon does not agree with older workers that any considerable amount of formic acid is produced, since he found that when oxalic acid is exposed with uranium sulphate to complete destruction no formic acid remained (actually 2 mg. total acidity was found on distillation). The fact that uranyl acetate gave no gas bubbles with formic acid in sunlight showed that his earlier result was not due to the destruction of formic acid previously produced, and what formic acid is found may probably be taken as arising by synthesis, from nascent CO, thus:—$CO + H_2O = H.COOH$.

Bacon carried out measurements of solar radiation by observing the rate of catalytic destruction of oxalic acid. Duclaux (1903) had made similar measurements with oxalic acid alone in Algeria, the interior of France, and at Helsingfors. He reached the strange conclusion that the active region of the spectrum was of increasing potency as one moved northwards. Berthelot and Gaudechon (1913) concluded that the effect of the catalyst (uranium salt) was to lower the light frequency needed to cause the reaction, just as an ordinary catalyst lowers the temperature required for a chemical reaction. Following up this line, Berthelot (1914) found that neither solid oxalic acid nor its solutions underwent any change when exposed to summer sunlight—in Paris apparently—for three months; from this he concludes that the near ultra-violet, $\lambda > 3000$ Å.U. is ineffective. Using a mercury arc and thin glass screen he obtained feeble radiations down to λ 2500 Å.U.; dry, solid oxalic acid gave (1) $(COOH)_2 = CO_2 + H.COOH$, with a little CO, presumed to come from further decomposition of H.COOH. In solution he concluded that secondary products were more abundant; thus the photolysis begins according to (1) and continues according to (2) $H.COOH = CO + H_2O$. No trace of formaldehyde was produced.

With an unscreened mercury arc he got hydrogen among his products, produced, he supposed, according to (3) $H.COOH = CO_2 + H_2$. With short exposures one has the superposition of (1), (2), and (3). After 16 hours equilibrium was reached according to (4) $(COOH)_2 = 2CO_2 + H_2$. Sometimes the proportion of hydrogen is too low, and then formaldehyde may be detected.

Even in the presence of the catalyst there is no mention of hydrogen being among the products of daylight photolysis. The reaction appears, therefore, to proceed according to equations (1) and (2), though this is in opposition to the views put forward by Bacon. In spite of the large amount of work done the mechanism of the reaction can hardly be considered to be perfectly known as yet.

Bacon, however, based his conclusions on experiments in daylight, and—whatever the products of the reaction—our method of calibration is based simply on the rate of destruction of oxalic acid.

A full account of earlier work has been given by Büchi (1924), who also carried out a careful physico-chemical study of the reaction. Lists of the known photo-chemical reactions have been given by Allmand (1925) and by Kistiakowsky (1928), and from these it may be seen that the photolysis of oxalic acid, with or without the addition of a catalyst, has been more exhaustively studied than any other reaction which can be followed readily and by simple means. Anderson and Robinson (1925) also used the method for measuring the radiation of lamps emitting ultra-violet light, and concluded that the amount of oxalic acid decomposed was proportional, within limits quoted further on, to the energy radiated over the whole ultra-violet range.

Before proceeding to the description of our own work we quote the valuable results obtained by Büchi, who summarises them as follows:—

1. The photolysis of the system of uranium salts with oxalic acid is a splitting up by light of the undissociated uranyl oxalate $[UO_2C_2O_4]$ or of the ion $[UO_2(C_2O_4)_2]''$.

2. The velocity of decomposition is independent of the oxalic acid concentration, and is constant as long as the oxalic acid is present in more than equimolecular proportion with respect to the uranium salt. For less than equimolecular concentrations of oxalic acid there is a photocatalysis which is nearly proportional to the concentration of oxalic acid. The inflection point is at equimolecular mixture.

3. The relatively great stability of the complexes is shown by, (*a*) the quantitative similarity of the photolysis for the systems of uranyl sulphate, nitrate, and oxalate with oxalic acid; and (*b*) the fact that the photolysis is independent of the presence of [certain] added substances—namely, O_2, HCl, H_2SO_4, H.CHO—provided these do not destroy the complex.

4. The acidity of the solution is decided by the proportion of formic acid produced (Antibasic) and that of uranous salts (Symbasic).

5. The main reaction, the destruction of oxalic acid in aqueous solution, is a spontaneous mass reaction.

6. For one light quantum absorbed one molecule of oxalic acid is destroyed, in conformity with Einstein's law. [See below, however.]

7. For the destruction of uranyl formate in sulphuric acid solution, in the initial stages a quantum value of $0{\cdot}7 \pm 0{\cdot}2$ is valid, that is for one quantum absorbed 0·7 molecule of uranous salt is formed and a corresponding amount of formic acid destroyed.

TABLE 1.

Wave length in Å.U.	Absorption.	Wave length in Å.U.	Absorption.
4072	100	4365	59
4104	97	4440	43
4167	93	4521	35
4229	80	4609	32
4295	67	4707	29

Table 1 shows the absorption of light of various wave lengths under the experimental conditions used by Büchi. It is clear that the absorption is complete in the extreme violet, incomplete in the blue, and increasingly so towards the blue green.

In connection with conclusion No. 3 (*b*), as to the rate being independent of the presence of added salts, mention should be made of the work of Müller, Jette, and West (1928), who found that certain substances inhibited the fluorescence of uranium solutions, and therefore, probably, affected their catalytic activity.

To prevent the interference of the formic acid, produced as a side reaction, with the estimation of oxalic acid by permanganate, Büchi used a solution containing 100 g. of $MnSO_4$ and 100 c.c. of concentrated H_2SO_4 in 1 litre. Of this 5–10 c.c. is added to the mixture, which is made up to 300 c.c. The titration is carried out at 85°–95° C.

Anderson and Robinson (1925) found that, when 25 c.c. of uranyl sulphate and oxalic acid solution was exposed in a rectangular fused silica vessel (the layer of solution being 1·5 to 2 cm. thick) to a mercury vapour arc, the rate of absorption of energy required to decompose 1 mg. of the acid in 30 minutes ranged from $4{\cdot}18 \times 10^5$ ergs per sec. at λ 2550 Å.U. to $5{\cdot}27 \times 10^5$ ergs per sec. at λ 3650 Å.U. These figures imply that the number of quanta absorbed per molecule of acid destroyed ranged from 20, at the shorter wave length, to 37, at the longer. This result differs widely from that obtained by Büchi.

They found the reaction to be of zero order, independent of the concentration of oxalic acid, and nearly so for that of uranium in dilute solution. The effect of temperature is not very great, the rate of reaction for a given illumination increasing by 3·5 per cent. for a rise of 10°. The solution they used was N/10 with respect to oxalic acid, and contained 4·27 g. of uranyl sulphate, $UO_2SO_4.3H_2O$, per litre. No explanation is given by them as to why this concentration of uranyl sulphate was selected, but it is not far from M/100, which contains 4·2028 g. per litre. Accordingly, from Büchi's conclusions (No. 2) it appears that, in Anderson and Robinson's mixture, the velocity of decom-

position would be independent of the concentration of oxalic acid until almost 90 per cent. of it had been used up.

As further evidence of the discrepancy which exists between the results of different workers as to the number of quanta absorbed per molecule of oxalic acid destroyed, we may instance the work of Boll (1913), who obtained the surprising result that, for the decomposition of oxalic acid in the presence of uranium nitrate by monochromatic radiation λ 2536 Å.U., each quantum corresponded to the decomposition of 50 molecules of acid.

These wide discrepancies seem to suggest that the sensitivity of the solution may possibly be affected by the presence of small quantities of some hitherto unrecognised catalyst or inhibitor. It would certainly seem to be desirable that, where the method is used for measuring daylight, the sensitivity of the solution, as made up, should be tested by comparison with some other photometer. For this purpose the photo-electric cell seems to be the most suitable. We give below an account of such a comparison and of some measurements of daylight, made by the uranium oxalate method.

Optical Conditions affecting the use of Tubes in Chemical Photometry.

Attention was called in some of our earlier papers (1925, p. 106, and 1926, 1, p. 180) to the optical conditions affecting the use of photometers whose windows consist of perfectly diffusing plane discs. It was there pointed out that we must specify exactly what we mean by the illumination at a given site, as several different definitions are possible. We were at that time only concerned with light travelling in a downward direction, which would contribute to the submarine illumination, but, in the general problem of measuring daylight, the reflected light may be of appreciable importance. This is especially the case over snow or water. Our definition of Total Illumination must, accordingly, be modified so as to include this reflected light.

The following nomenclature is adopted below. V is the vertical illumination on a horizontal surface, and is generally composed of the vertical component of pure sunlight, V_s, plus that of diffuse skylight, V_d. For simplicity, the sky is assumed to be equally bright all over, though this is, usually, only approximately true. V_r is the reflected vertical illumination which would be received on an inverted window, assumed to be small enough not to shade appreciably the ground below it. H is the horizontal illumination on a plane vertical surface. Using the suffixes in the same sense as before, we may write $H = H_s + H_d + H_r$. It is evident that, when the sun is shining so that H_s is not zero, the value of H will depend on the orientation of the receiving surface. M is the illumination on a surface set at such an angle as to catch the maximum flux of light. If the site is an open one, and the sun is not shining, this surface will be horizontal, so that, under these conditions, $M_d = V_d$. When the sun is shining the surface must be set nearly, but not quite, perpendicular to its rays, so that the relation between M and the other quantities is rather complex.

I, the total illumination at the given point, cannot be received directly on any single plane surface. It is best defined as $\int_0^{4\pi} id\Omega$ where $id\Omega$ is the illumination due to a small pencil of rays of solid angle $d\Omega$ on a small area normal to the axis of the pencil. As before, we may write $I = I_s + I_d + I_r$, where I_s is the illumination from the small angle comprising the sun's disc, $I_d = \int_0^{2\pi} id\Omega$ is that due to the sky, the integral being taken over the remainder of the upper hemisphere, and, for a uniform sky, being equal to $2\pi i$, and I_r is the same integral taken over the lower hemisphere, the value of i in this case being that for the reflected light, which may for convenience be taken as being uniformly distributed. I may be measured, as mentioned below, by means of a photometer whose absorbing surface is a complete sphere. This condition is most easily fulfilled by the use of a photo-sensitive liquid in a spherical flask.

It is easy to see that the following relations hold between the quantities defined above:—(1) $I_s = V_s \operatorname{cosec} a = H_s \sec a$, where a is the altitude of the sun, and H_s refers to a vertical surface set in azimuth normal to the sun's rays; (2) $I_d = 2V_d = 4H_d$; and (3) $I_r = 2V_r = 4H_r$.

When a photo-sensitive liquid is exposed to light in a transparent tube, whose length is large compared with its diameter, the rate of chemical action produced by a given illumination will vary greatly according to the angle between the axis of the tube and the light. The magnitude of this variation will depend on whether the liquid absorbs the light strongly, or only slightly, as, in the latter case, the reduction in effective area caused by obliquity of illumination will be partially compensated by the increased length of path of the light through the liquid. This compensation is never complete, and becomes very ineffective at large angles of obliquity, as, owing to refraction, the light in the liquid can never make a smaller angle with the axis of the tube than 41·5°.

If the liquid absorbs strongly, increase of optical path in the liquid does not add to the rate of action, as all the light is absorbed even in the shorter path. In this case the flux of light entering the tube is the sole determining factor, so that the rate of action would be proportional to the sine of the angle between the axis of the tube and the light, if it were not for the increased reflection loss at the outer surface, which occurs at large obliquities (see 1926, 1, p. 184).

It is, perhaps, legitimate to assume, for the sake of simplicity, that this reflection loss would, in practice, about balance the partial compensation for obliquity caused by the lack of complete absorption in the liquid, and to treat the tube as a perfectly absorbing cylindrical surface, whose length, L, is so large compared with its diameter, D, that the ends may be neglected. When such a cylindrical absorbing surface is employed in place of the plane surface used in our photo-electric photometers, the illumination measured is the mean for all directions normal to the axis of the cylinder, instead of the illumination

perpendicular to a plane. This must be remembered in comparing the results obtained with the two different types of photometer. Thus, when the tube is exposed vertically it measures the mean horizontal illumination for all azimuths, $\bar{H}$, the total light flux received being

$$\pi LD(H_d + H_r) + LDH_s, \text{ or } \pi LD\bar{H}, \text{ where } \bar{H} = H_d + H_r + \frac{H_s}{\pi}.$$

It is obvious that, where a is large, direct sunlight does not contribute very much to $\bar{H}$, as H_s (i.e. $I_s \cos a$) is small. This must be remembered when interpreting Hill's results, obtained in such different latitudes as London, Davos, and Assuan (1927).

If the sun is not shining, so that H_s is zero, the light received by the tube is not affected by tilting it to any angle, as the increase of light on the upper side is exactly compensated by the decrease on the lower side. If the tube is placed horizontally its reading, for diffuse light, is still the same as before, so that the rate of action corresponds to a light flux

$$\pi LD(H_d + H_r) \text{ i.e. to } \frac{\pi LD(V_d + V_r)}{2}.$$

If the sun is shining, its contribution to the light flux received by a horizontal tube will depend on the azimuth of the latter, ranging from LDV_s (i.e. $LDI_s \sin a$) to LDI_s, according as the axis of the tube is in, or perpendicular to, the sun's azimuth. Thus, dividing, as before, by the area πLD, we find that the mean vertical illumination recorded by the tube varies from

$$\frac{V_d + V_r}{2} + \frac{V_s}{\pi} \text{ to } \frac{V_d + V_r}{2} + \frac{I_s}{\pi}.$$

according to the azimuth of the tube.

If a tube containing uranyl oxalate is exposed to bright light, the rate of generation of gas is so great that the gas must be allowed to escape. It is not very easy to arrange for this to happen without loss of liquid if the tube is placed horizontally. It is, accordingly, most convenient to adopt the vertical position as a standard practice, though in some of the measurements described below the tubes were placed at a small angle (about 15°) to the horizontal.

When a tube is standardised by exposure to any small source, such as a lamp, under such conditions that reflected light from the walls of the room is unimportant, the effective area of the tube is only LD, while the same tube, when used to measure the mean horizontal illumination, $\bar{H}$, has an effective area πLD. The mean illumination due to the lamp over the whole tube is, thus, only $1/\pi$ of the direct illumination on one side of the tube, and this factor must be introduced into the standardisation if we wish to use the tube to measure the mean illumination. This does not appear to have been done in Hill's work, so his figures are really a measure of $\pi(H_d + H_r)$, i.e. of $\frac{\pi}{4}(I_d + I_r)$ as far as diffuse skylight and reflected light are concerned. For pure sunlight his

method measures H_s (i.e. $I_s \cos \alpha$), or I_s according as his tubes were exposed vertically, or normal to the sun's rays. Thus, the fact that the diffuse skylight produced more action on his tubes than the direct sunlight does not necessarily mean that the same would be true for the ultra-violet light falling on a plane, or nearly plane, surface.

If the solution were exposed in a spherical flask of radius R, which it just filled, the effective absorbing area for a pencil of light at any angle would be πR^2, so that, if the flask were standardised by exposure to a lamp and used for daylight without the introduction of any factor (such as π for the tube above), the result obtained would be I, as defined above. In this case the mean illumination on the surface of the flask would only be $I/4$, since the total area is $4\pi R^2$.

It is well to bear in mind, when considering the physiological aspects of daylight photometry, that the rate of action on a definite area of skin or leaf in an approximately fixed position depends on the intensity of illumination on that area, which may be V, H, M, or some intermediate value, according to the orientation of the surface. The total action on the whole body or plant is, however, nearly proportional to I.

If, when taking a "Sun Bath" the subject changes his position in such a way as to expose his whole body approximately uniformly to the sun, the average illumination on any part of it is approximately $I/4$.

There would seem, therefore, to be much to be said in favour of the use of spherical flasks for the exposure of photo-sensitive liquids, so as to obtain a direct measure of I.

Preparation and Exposure of the Solution.

Uranyl sulphate, as purchased, is of indefinite composition, having lost water. We accordingly crystallized it in a desiccator over sulphuric acid, and selected crystals which showed no sign of efflorescence.

In making up the solution we employ the proportions used by Anderson and Robinson, namely, 6·3 g. of pure crystalline oxalic acid and 4·27 g. of uranyl sulphate, $UO_2SO_4.3H_2O$, made up to 1 litre, and stored in a brown bottle; it was titrated against deci-normal permanganate taking 10 c.c. of the mixture, 10 c.c. of dilute sulphuric acid, and 100 c.c. of boiling water. The sulphuric acid used was 1 volume of concentrated acid diluted with 3 volumes of water, and to this, while still hot, permanganate was added drop by drop as long as the impurities in the acid continued to decolorize the solution. Use was not made of the addition of the manganous sulphate solution recommended by Büchi, because we were unaware of his work till our own was well advanced. The end point appears to be quite a sharp one, even without the manganous sulphate, but a little formic acid is estimated along with the oxalic.

An attempt was made to increase the rapidity, with which accurate analyses of the oxalic acid used up could be determined, by measuring the electrical conductivity of solutions, analysed after insolation. It was found, however, that

the results obtained were very erratic, even when by shaking with air, or by warming and shaking, the carbon dioxide produced had been almost entirely removed. The values were found to depend upon the time the solution had remained in contact with the platinised electrodes, and there may be some action upon the formate produced. Better results might be obtained with bright electrodes, but as they could scarcely be of a reasonably high degree of accuracy the attempt was not made.

It also appeared possible that indicators could be used to observe the reduction in hydrogen ion concentration due to the destruction of oxalic acid, since the carbon dioxide produced is a much weaker acid, and, being gaseous, mostly escapes. The Clark and Lubs series of sulphone-phthalein indicators were found to be perfectly stable when exposed in quartz tubes for one hour to bright sunlight. When exposed in presence of oxalic acid, or of the mixture, the indicator suitable for high acidity, thymol blue, was decolorized irreversibly. It might be possible to get the required information by adding the indicator subsequently, but the value of a visible change while the exposure is in progress would be lost.

Numbered quartz tubes, 13 cm. long by 1·3 cm. internal diameter, were, at first, exposed horizontally, as described in Table 2. It was found, however, that the evolution of gas forced out the rubber stoppers, so in some subsequent exposures the open tubes were placed on cork supports, lying as nearly horizontal as was possible without spilling the contents, 10 c.c. of the mixture. The angle with the horizontal was 14–16 degrees, and if the sun was shining the tubes were placed so as to point and slope towards it. Table 2 shows that exposures thus made give results which are usually consistent to within 2 per cent., though, if the amount of oxalic acid destroyed is very small, the divergence from the mean may amount to 4 per cent.

[Table 2.

TABLE 2.

Exposure of numbered quartz tubes (placed horizontally, A, or at 15° with a horizontal plane, B and C) containing uranyl oxalate mixture, 10 c.c. The second, fourth, and sixth columns show the volume of deci-normal acid decomposed by daylight, on the south parapet of the flat roof of the Marine Biological Association's Laboratory, at Plymouth. The third, fifth, and seventh columns show the percentage deviations from the mean. A exposed 15 min. from 11.2 G.M.T., 1/5/'28. B exposed 60 min. from 3.7 G.M.T., 1/5/'28. C exposed 60 min. from 1.52 G.M.T., 4/5/'28. A and B, sunny exposures, tubes pointing to sun. C, dull, uniform grey sky.

No.	A.		B.		C.	
	c.c.	%	c.c.	%	c.c.	%
1	2·90	0·0	9·17	+ 2·0	2·00	− 2·5
2	—	—	8·92	− 0·8	2·06	+ 0·5
3	—	—	9·08	+ 1·0	2·03	+ 1·0
4	2·82	− 2·8	8·90	− 1·0	1·97	− 4·0
5	—	—	9·09	+ 1·1	1·99	− 3·0
6	—	—	8·83	− 0·7	2·10	+ 2·0
7	2·95	+ 1·7	8·90	− 1·0	2·06	+ 0·5
8	—	—	9·00	+ 0·1	2·10	+ 2·0
9	—	—	9·00	+ 0·1	2·12	+ 3·5
10	2·88	− 0·7	9·02	+ 0·3	2·04	− 0·5
11	—	—	8·99	0·0	2·13	+ 3·5
12	2·95	+ 1·7	8·99	0·0	2·00	− 2·5
Mean	2·90	—	8·99	—	2·05	—

Photo-electric Standardisation of the Tubes.

It has been pointed out that it is generally most convenient to expose the solution in vertical tubes, so as to measure the mean horizontal light. To standardise the tubes in this position would require readings to be taken with a vertical photo-electric photometer window in a number of azimuths. There is no reason why this should not be done, and this method is to be recommended. Our initial standardisation, however, has been made with a horizontal window, as is our usual practice, the tubes being set as nearly horizontal as the necessity for allowing the escape of gas would permit (see Table 3). This involved tilting the tubes to an angle of about 15°, the lower end pointing, in azimuth, towards the sun.

Table 3.

Determinations of hourly rates of decomposition of uranyl oxalate mixture and of rate per thousand metre candles illumination. Exposures made in standard quartz tubes (set at 15° to horizontal, sloped towards and pointing to sun) on front parapet of M.B.A. Laboratory roof, Plymouth, save for two made in forenoon of May 30th, on a wall at Antony, Cornwall, exposed to full daylight. ‡ Denotes tube suspended vertically, cork removed; for other vertical exposure rates see Tables 4 and 5.

Date.	G.M.T.	Conditions.	α.	β.	V. k.m.c.	F.	$V.F.$ k.m.c.	Rate of Decomposition. c.c. per hr.	c.c. per hr. per k.m.c.	U. k.m.c.
May 1.	11.2–11.17 a.m.	Clear sun, some clouds, wind E.	—	—	—	—	—	11·60	—	51·5
„ „	3.7–4.7 p.m.	Do. fewer clouds	—	—	—	—	—	8·99	—	40
„ 4.	1.52–2.52 „	Uniform dull sky, wind N.N.W.	—	1·0	14·7	0·7	10·3	2·05	0·20	9·1
„ 10.	2.0–2.30 „	Clear sun, high haze, wind light, S.E. ...	50°	2·5	84	0·625	52·5	11·38	0·215	50·5
„ „	2.30–3.0 „	Do. Do. ...	45°	2·3	77	0·64	49	10·96	0·225	49
„ „	4.0–4.30 „	Do. Do. ...	32°	2·2	55	0·665	36·5	9·14	0·25	40·5
„ „	4.30–5.0 „	Do. Do. ...	27°	2·0	45	0·685	31	7·78	0·25	34·5
„ 30.	5.40–8.40 a.m.	Entirely overcast	—	1·0	—	—	—	2·05	—	9·1
„ „	8.40–11.40 „	Very murky, rain, clearing	—	1·0	—	—	—	2·63	—	11·7
July 10.	2.15–2.55 p.m.	Sun hot, high light cloud, wind light, S. ...	—	—	—	—	—	10·05	—	44·5
„ „	2.15–2.55 „	Do. Do. ...	—	—	—	—	—	9·98‡	—	44·5‡
„ 18.	12.15–12.45 „	Sun hot, sky clear, calm	60°	4·6	116	0·585	68	13·52	0·20	60
Aug. 2.	2.57–3.27 „	Clear sun, a few small fleecy clouds, wind light, E.	—	—	—	—	—	12·16	—	54
„ „	3.17–3.47 „	Do. Do.	—	—	—	—	—	12·14	—	54
„ „	3.1–3.31 „	Do. Do.	—	—	—	—	—	11·00‡	—	49‡
„ „	3.31–4.1 „	Do. Do.	—	—	—	—	—	10·54‡	—	47‡
„ „	4.1–4.46 „	Do. Do.	—	—	—	—	—	9·12‡	—	40·5‡
„ „	4.46–6.1 „	Do. Do.	—	—	—	—	—	6·58‡	—	29‡

In deducing the mean illumination acting on the tubes from the reading of the photometer, which contained a potassium vacuum cell, we must first divide the vertical illumination, V, indicated by it into the parts due to pure sunlight and diffuse skylight, respectively. This is most conveniently done by finding the ratio, β, of the photometer readings when the window is fully exposed, and shaded from direct sunlight by means of a small object, respectively. Numerous determinations of β have been made in the course of our work. It affords information as to the general character of the light. Thus, at Plymouth strong sunlight gives $\beta = 3$, or over; moderate, 2; weak, 1·5; when the sun is not shining $\beta = 1$.

Having found the vertical illumination due to diffuse skylight by dividing the total vertical illumination by β, we must take the mean of this and the estimated value of the reflected light, which acts on the under surface of the tube but does not affect the horizontal photometer window at all. As the tubes were exposed on the limestone parapet of the laboratory roof, we may, perhaps, assume an albedo of 40 per cent., so that the mean diffuse illumination acting on the tube may be taken as $(1/2\beta + 0{\cdot}2)\ V$, the tilt having no effect for diffuse illumination.

To this must be added the mean illumination due to direct sunlight, remembering that, owing to the tilt of the tube, the effective altitude of the sun is $a + 15°$, where a is the real altitude. Thus, since the area of the tube exposed to sunlight is only $1/\pi$ of its total area, the sunlight illumination is obtained by multiplying V by

$$\frac{(\beta - 1)\sin(a + 15°)}{\beta\pi \sin a},$$

and in order to find the total mean illumination on the tube we must multiply V by a factor,

$$\frac{1}{2\beta} + 0{\cdot}2 + \frac{(\beta - 1)\sin(a + 15°)}{\beta\pi \sin a},$$

which is designated F in Table 3. It will be seen that F varies from 0·585 to 0·70. The values for the rate of decomposition per thousand metre candles, given in the second last column, are obtained by dividing the figures in the preceding column by the effective illumination FV.

The same result was obtained for the rate of decomposition per thousand metre candles on a dull day (May 4) and on a very bright day with clear sun (July 18). On the other hand, the rate was somewhat higher on May 10, which was of an intermediate character, and rose further as the sun declined. Without more observations it is not safe to draw any definite conclusions from these variations, which may be due to differences in the character of the light, the tubes being relatively more sensitive to the ultra-violet than the photo-electric cell.

As a result of these comparisons it has been assumed that the decomposition of 0·225 c.c. of deci-normal acid per hour corresponds to a mean illumination

on the tube of one thousand metre candles (1 k.m.c.). The figures in the last column, headed U, are the illuminations so found from the decomposition of the uranyl oxalate solution. In those cases in which the tube was vertical U is identical with $\bar{H}$, the mean horizontal illumination.

TABLE 4.

Hourly rates of decomposition of uranium oxalate solution exposed in stopperless tubes, of quartz, Q, or Monax glass, M, and suspended so as to swing about a mean vertical position on the topping lift leading from the mast to the end of the boom on S.S. Salpa. The first set relates to a run made on Aug. 17, 1928, from International Hydrographic Station E 3, off Ushant to Plymouth; the second set relates to a run from Plymouth to E 1 and back, on Sept. 18. On Aug. 17 the sky was mainly covered with light clouds till 10 a.m., sun clear 11 a.m., with high haze. On Sept. 18 there was fog till 10 a.m., then sunshine, with β 1·91 at 10.30 and β 2·24 at 1.40.

August 17, 1928.				September 18, 1928.					
Mean G.M.T.	Exposure. min.	Q. c.c. per hr.	$\bar{H}$. k.m.c.	Mean G.M.T.	Exposure. min.	Q. c.c. per hr.	$\bar{H}$. k.m.c.	M. c.c. per hr.	$\frac{Q}{M}$.
5.8* a.m.	—	—	—	5.56* a.m.	—	—	—	—	—
6.44 „	192	2·95	13·1	7.14 „	157	1·08	4·8	1·06	1·01
9.30 „	145	3·94	17·5	9.19 „	92	5·38	24	4·99	1·08
11.20 „	75	7·58	33·5	10.28 „	46	8·56	38	7·49	1·14
12.20‡ p.m.	45	11·40	50·5	11.14 „	46	9·81	43·5	8·79	1·12
1.5 „	45	11·25	50	12.0 noon	47	10·23	45·5	9·17	1·12
1.50 „	45	8·57	38	12.48 p.m.	48	9·70	43	8·08	1·20
2.45 „	60	8·88	39·5	1.37 „	51	9·34	41·5	8·08	1·15
3.45 „	60	9·07	40·5	2.30 „	53	9·34§	41·5	8·17	—
4.50 „	75	7·30	32·5	3.26 „	60	5·65	25	4·60	1·19
6.30 „	120	2·22	9·9	4.30 „	67	3·39	15·0	3·12	1·09
7.32† „	—	—	—	5.44 „	82	1·09	4·8	0·83	1·31
			—	6.25† „	—	—	—	—	—
Mean			25·8	Mean			23·6	Mean	1·14

* Sunrise. † Sunset. ‡ Local apparent noon, which was at 12.11 p.m. on Sept. 18. § Calc. from value of M, as a spare M tube was accidentally exposed instead of Q.

Diurnal Variation in the Mean Horizontal Illumination.

Table 4 shows the results of measurements made at sea with a vertical tube at different times throughout two days. The first three readings on August 17 are probably too low, as the tubes were over-exposed, so that over 90 per cent. of the oxalate was decomposed, and beyond this the rate of decomposition is proportional to the concentration, instead of being independent of it. Similar observations have been made by Marshall and Orr (1928). They used tubes, apparently of glass, but their results seem to refer to the vertical illumination.

The difference between exposures in thin glass and in quartz is shown in the results for September 18, and the ratio Q/M has a mean value of 1·14. There seems, therefore, to be no objection to making the exposures in glass for ecological purposes. The quartz tube values of Table 4 are plotted in the graph, together with a few similar results obtained on various other dates. In finding the values of $\bar{H}$ given in the Table and the graph it has been assumed that the decomposition of 0·225 c.c. of acid per hour corresponds to one thousand metre candles. The low values at 9.30 and 11.20 a.m. on August 17 are plotted, but disregarded in drawing the graph for the day. They, however, affect the daily mean, given in Table 4, which is found from the illuminations and time intervals given in the table. The mean found from the graph is about 28·3.

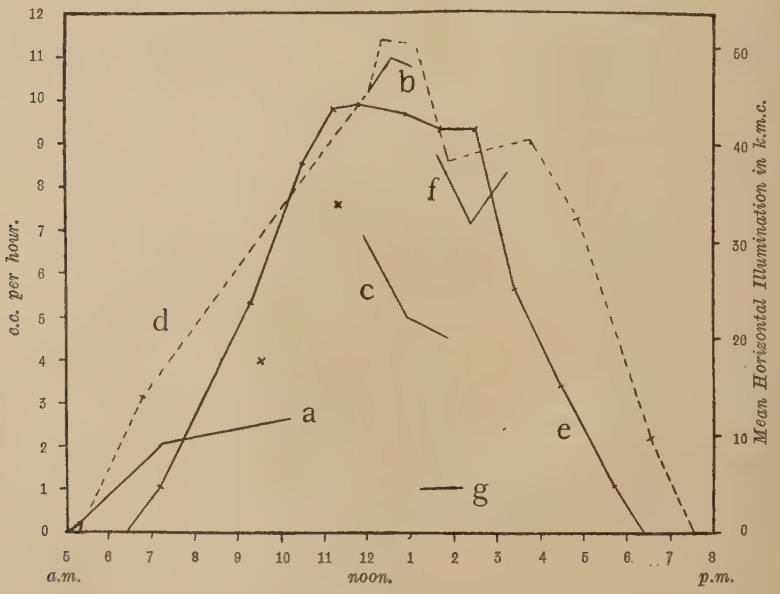
TABLE 5.

Comparative readings made at sea of the mean horizontal illumination $\bar{H}$, as measured by uranyl oxalate tubes hung from the rigging so as to swing freely about a vertical position, with the vertical illumination V, indicated by a vacuum potassium photo-electric cell mounted on gimbals on the deck and read at frequent intervals during the exposures of the tubes, and the mean horizontal illumination $\bar{H}_c$, found by calculation from V. $\bar{H}_c$ does not include any allowance for light reflected off the water, so the ratio $\bar{H}/\bar{H}_c$ should be considerably greater than unity. In finding $\bar{H}$, it has been assumed, in accordance with the results of Table 3, that the decomposition of 0·225 c.c. of decinormal acid per hour corresponds to one thousand metre candles (1 k.m.c.).

Date.	G.M.T.	α °	β.	V k.m.c.	$\bar{H}_c$ k.m.c.	$\bar{H}$ k.m.c.	$\bar{H}/\bar{H}$
July 4.	11.53 a.m.–12.38 p.m.	63	6·0	125	27·2	46·7	1·71
„ 11.	11.32 „ –12.2 „	62	3·0	116·5	32·5	—	—
„ „	12.2 p.m.–12.32 „	62	2·5	108	32·6	41·7	1·28
„ „	12.32 „ – 1.2 „	61	2·5	116	35·5	52·8	1·49
„ „	1.2 „ – 1.32 „	59	2·7	99·5	30·3	—	—
„ „	11.32 a.m.– 1.32 „	61	2·7	110	32·7	45·5	1·39
„ 23.	11.44 „ –12.14 „	59	4·5	118·5	30·8	45·6	1·48
„ „	12.14 p.m.–12.44 „	59	4·5	118·5	30·8	48·7	1·58
„ „	12.44 „ – 1.16 „	58	4·0	117	32·0	48·0	1·50
„ „	11.44 a.m.– 1.16 „	59	4·3	118	31·2	47·4	1·52
Aug. 8.	11.23 „ –12.23 „	55	1·5	52	21·2	30·6	1·44
„ „	12.23 p.m.– 1.23 „	55	1·3	40·5	17·7	22·2	1·26
„ „	1.23 „ – 2.23 „	51	1·3	37·8	16·8	20·0	1·19
„ „	11.23 a.m.– 2.33 „	54	1·4	43·4	18·6	24·2	1·30
„ 29.	11.56 „ –12.42 „	49	4·0	106·5	35·5	44·3	1·25
„ „	12.43 p.m.– 1.27 „	47	4·0	100·5	35·0	44·7	1·16
„ „	1.27 „ – 2.15 „	42	4·0	93	36·3	40·4	1·23
„ „	11.56 a.m.– 1.27 „	48	4·0	103·5	35·2	43·2	1·23
„ „	11.56 „ – 2.15 „	46	4·0	100	35·6	43·1	1·21
Sept. 18.	2.3 p.m.– 2.56 „	33	2·0	65	32·2	41·5	1·29
„ „	2.56 „ – 3.56 „	27	1·7	33·7	18·6	25·1	1·35
„ „	2.3 „ – 3.56 „	30	1·8	48·5	25·4	32·5	1·28
Oct. 2.	1.9 „ – 2.0 „	32	2·0	66·5	33·5	38·8	1·16
„ „	2.1 „ – 2.52 „	28	2·0	57·5	31·6	31·9	1·01
„ „	2.52 „ – 3.26 „	24	2·0	52	31·6	37·1	1·17
„ „	1.9 „ – 3.26 „	28	2·0	59	32·2	35·8	1·11
Nov. 30.	12.35 „ – 2.48 „	15	1·0	7·3	3·6	4·3	1·19

Comparison of $\bar{H}$ as found by Tubes with V as found by Photo-electric Cell.

During our measurements of the absorption coefficient of sea water by means of photo-electric cells measuring the vertical illumination some comparative observations were made with uranyl oxalate tubes, suspended in the rigging so as to hang vertically and measure the mean horizontal illumination, $\bar{H}$. The results are shown in Table 5, and plotted in the figure. It will be seen that the ratio of $\bar{H}$ to the value of the mean horizontal illumination, $\bar{H}_c$, calculated from V, ranges from 1·71 to 1·01, the average value of the ratio being 1·31. As $\bar{H}_c$ does not include any reflected light, this ratio should be a measure of the contribution of the latter to the horizontal illumination. The value found for the average appears to be reasonable, but the variations are too large for the method to be considered a satisfactory one for the measurement of this reflected light, which could obviously be done better by using horizontal and vertical photometers of the same type. The general agreement, however, between these measurements and the standardisation recorded in Table 3 is quite satisfactory.



The ordinates represent hourly rates of consumption of the uranyl oxalate solutions at the mean times shown by the crosses, the abscissae denoting hours, G.M.T. Dotted line (d) from data of 17/8/'28, on S.S. Salpa, run from Ushant, dawn, to Plymouth, 5.30 p.m., then in Sutton Pool. Full line (e) run from Plymouth out 22 miles to International Hydrographic Station E 1 and back. Curve (a), for May 30th, open site on hill at Antony, Cornwall. Other curves from exposures at E 1, on dates as follows:—(b) July 23rd; (c) Aug. 9th; (f) Oct. 2nd; (g) Nov. 30th.

The very high value of the ratio $\bar{H}/\bar{H}_c$ recorded in the first line is possibly due to an error in β, as the value 6 is quite exceptional, and may, possibly, be due to the accidental shading of some skylight along with the sunlight in the determination of β. The assumption that 5/6ths of the total vertical illumination is due to sunlight leads, as explained on p. 327, to a very low estimate of the mean horizontal illumination. There was a general tendency for $\bar{H}/\bar{H}_c$ to fall as the autumn and winter approached. This is probably due, partly to a reduction in the relative intensity of ultra-violet light, and partly to a fall in the sensitivity of the uranyl oxalate solution with fall in temperature.

Summary.

The rate of decomposition of a solution containing 6·3 g. of crystalline oxalic acid and 4·27 g. of uranyl sulphate, $UO_2SO_4.3H_2O$, per litre was compared with the reading of a potassium vacuum photo-electric cell which had been standardised by means of an open carbon arc.

It was found that, when due allowance had been made for the fact that the absorbing surface of the cell was plane and that of the solution approximately cylindrical, 10 c.c. of the solution exposed in a quartz tube about 13 cm. long by 1·3 cm. internal diameter, showed a rate of decomposition of 0·225 c.c. per hour for an illumination of 1,000 metre candles.

When glass tubes are used the reduction in the ultra-violet light causes a reduction in the rate of action, Monax glass tubes requiring 1·14 times as great an exposure as quartz. This should not prevent the use of glass tubes for ecological work.

Measurements of the mean horizontal illumination were made at sea over two complete days by means of tubes suspended in the rigging, the average for the period from sunrise to sunset being 25,800 metre candles on August 17, and 23,600 metre candles on September 18, 1928.

Comparisons of the mean horizontal illumination at sea found in this way on various dates with the vertical illumination as measured by readings of a photo-electric cell agreed well, on the average, with the ratios to be expected theoretically when allowance was made for the effect of light reflected off the water.

It is pointed out that the usual practice of exposing photo-sensitive liquids in vertical tubes measures the mean horizontal illumination. If the liquid is exposed in a spherical flask the total illumination can be measured. This may be desirable for some purposes.

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No. 27.

THE INSECT VECTORS OF THE LEAF-ROLL DISEASE OF THE POTATO.

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AND

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The infectious nature of the leaf-roll disease of the potato, and the spread of the disease in the field from affected plants to healthy plants in their immediate vicinity, were first established by Quanjer *et al.* (13). This was subsequently confirmed by Murphy and Wortley (8), and later by others.

The agency by which infection is conveyed from plant to plant was discovered by Oortwijn Botjes (11). This worker showed that when aphides (he used a combination of *Aphis rumicis* L. and *Myzus persicae* Sulz.) were transferred under controlled conditions from diseased to healthy plants, the latter in due time developed symptoms of disease. It was also believed that capsids ("Wanzen") could probably convey infection, and that there was a possibility of transference below ground level.

The part played by aphides was independently confirmed by Schultz and Folsom (14). Using *Myzus persicae* Sulz. (in one experiment in combination with *Macrosiphum solanifolii* Ashmead), infection was regularly secured on a large proportion of the experimental plants under controlled conditions. In a later publication, the same workers (15) record the transference of leaf-roll in one experiment by "aphides" without giving further particulars; and in a further paragraph state that "*Macrosiphum solanifolii* Ashmead transmitted mild mosaic, both alone and in combination with leaf-roll." It is probable that they consider that both the aphides mentioned are equally capable of transmitting leaf-roll, for they state in a subsequent paper (16) that "it is well known from previous studies by the writers and others that *Macrosiphum solanifolii* and *Myzus persicae* transmit virus diseases of the potato and other cultivated plants." Miss Patch (12) also states that *M. solanifolii* is known to carry leaf-roll. Incidentally, Schultz and Folsom (15) secured negative results with flea-beetles (*Epitrix cucumeris* Harris) and Colorado potato beetles (*Leptinotarsa decemlineata* Say).

The earlier work of Schultz and Folsom was marked by uniformly successful transference of leaf-roll by means of the aphides they used. This, as will be

seen, was not the case elsewhere. In 1925 (16), however, they also found that aphides sometimes do not transmit various virus diseases of the potato (including leaf-roll) under apparently favourable conditions. The identity of the aphides used in this case is not given.

The successful transfer of leaf-roll by means of *Myzus persicae* was recorded by Murphy (7) in 1923, infection being conveyed from, and to, the sprouts of unplanted tubers. In subsequent experiments Murphy and M'Kay (9 and 10) found that aphides sometimes transferred infection from leaves or sprouts, but more usually failed to do so. The aphides principally used in these later experiments were *Macrosiphum solanifolii* and *Myzus pseudosolani*, both of which occasionally transferred the disease. (See below for further details.)

Partly in consequence of these experiments, and partly on account of the observed spread of leaf-roll in the field where aphides were apparently scarce or absent, while other insects were common, the conclusion was come to that other vectors were probably involved. Evidence (7) was presented to show that capsids (*Calocoris bipunctatus*) and jassids (*Typhlocyba ulmi*) could carry infection from plant to plant. In a later paper (10) further positive evidence concerning *C. bipunctatus* was given.

Folsom, Schultz, and Bonde (4), in a further paper dealing with potato degeneration diseases, came to the conclusion, as a result of failure to correlate prevalence of infection with aphis infestation, that there were other insect transmitters involved. These remarks appear, however, to apply particularly to "mild mosaic" and "spindle tuber," and not to leaf-roll. These workers noticed that the spread of the various virus diseases of the potato was not uniform under the same conditions, indicating that "they probably do not transmit similarly." Gardner and Kendrick (5), also, have recently pointed out that leaf-roll spreads more readily than mosaic (in some varieties at least) in Indiana, while the reverse is the case in Maine (4). As is well known, there are in these Islands certain "leaf-roll districts" where this disease is in the ascendant, while elsewhere (and particularly in the best seed-potato districts) mosaic is much more common. Glasnevin is situated in one of the former areas, and we have noticed for years that if any disease develops in healthy isolated plants it is generally leaf-roll.

One of the earlier ideas concerning the propagation of leaf-roll was that the infection was conveyed through the soil (13, 6, and 11), and Whitehead (18) submitted evidence of soil transmission in Wales in 1921, while in 1922 both aerial and soil transmission are believed by him to have taken place. Folsom, Schultz, and Bonde (4) also recently stated that transmission by soil contact may be a possibility, as does Atanasoff (2).

Elze (3) in 1927 reviewed the whole field of virus diseases transmission in his thesis, and submitted the results of much experimental work on insect transmission of the virus diseases of the potato. So far as leaf-roll is concerned, he found that the disease was transmitted in controlled experiments in cages and under glass by the following:—*Myzus persicae, M. pseudosolani, Aphis*

rhamni, *Aphis fabae* (possibly), *Eupterix auratus*, *Lygus* sp., *Psylliodies affinis*, and (working below ground level) larvae of *Tipula paludosa*. The two first mentioned aphides also conveyed infection from tuber to tuber. Infection was most readily conveyed by aphides, and of these, *Myzus persicae* had the greatest infecting power. *Macrosiphum solanifolii* was not included in the experiments.

After the present paper was written, Kenneth Smith (17) published an account of his work on the insect transmission of leaf-roll. He secured uniformly negative results when the following insects were transferred from diseased to healthy sprouts:—*Calocoris bipunctatus*, *Lygus pabulinus*, *Eupteryx auratus*, *Chlorita viridula*, *Psylliodes affinis*, *Macrosiphum gei*. (*Eupteryx auratus* was also tried in the foliage.) In contrast with this, leaf-roll was transmitted with great regularity by *Myzus persicae* in two successive years.

The credit for the discovery of the relationship existing between *Myzus persicae* and leaf-roll belongs to Smith. As will be seen, our own independent results also emphasize the extreme facility with which this insect can convey leaf-roll infection. We are not, however, at present disposed to believe that an exclusive relationship exists between the virus and this particular insect.

The existing position is, as will be seen, that aphides, or certain of them, are well known to be capable of conveying leaf-roll from plant to plant or sprout to sprout. Some workers appear to have had equal success with all the aphides they used, or at least they do not differentiate between them; others, while comparatively successful with several, find that one species transmits infection more regularly than the others; while in other cases practically only one species has been found to transmit. At the same time there has evidently been growing up a body of opinion which doubts if all the disease dissemination to be observed in the field can be attributed to aphides. The present writers were at one time of this opinion, but as a result of the work now to be described, have been forced to take a modified view. There are two distinct questions involved—the technical one of the identity of the vectors which are capable under any conditions of conveying leaf-roll from plant to plant, no matter in how few cases, and the question of more practical concern, as to which insect (or insects) is principally responsible, either universally or in any particular place.

Experimental Transmission of Leaf-roll by means of various Aphides (1922–1928).

An account of most of the experiments concerning the insect transmission of leaf-roll which are here brought together has not been published, but some published work must be included to arrive at a proper understanding of the situation. The experiments were carried out during the years 1922 to 1928, for the most part with plants grown in pots under individual insect-proof cages made of calico, or in insect-proof houses. The tubers were the produce of healthy plants (in later years of proved virus-free plants) usually raised in insect-proof houses, and in every case a portion of each tuber was grown without insect infestation as a control. In no case was leaf-roll detected in these

control plants. In some of the experiments, in which aphides were placed on the sprouts of unplanted tubers, the latter were planted in the open, with individual controls on each (see Table I). These experiments were usually conducted on such a scale as to render individual cages impossible. It is quite possible, however, to conduct exact experiments in this way, for if infection through the sprouts takes place, *secondary* leaf-roll appears in May and June, about one month before any primary leaf-roll develops as a result of insect-borne infection through the foliage. The original experiment of 1922 was carried out in this way. Atanasoff (2) later strongly recommended this procedure not only for leaf-roll, but for streak and other diseases.

The aphides used were raised from a single colony (in 1925 and 1928 from a single female), and were propagated on the sprouts or foliage of healthy (in later years, proved virus-free) tubers or plants which were afterwards grown to maturity. In cases in which the insects originated from non-solanaceous plants such as rose and loganberry in early spring, no special precautions were taken to prove that virus infection was absent, and none was found necessary. Where they originated on potato sprouts (after 1922) the stock was raised from a single nymph produced in a glass vessel according to the method already described by us (10), which has always given a virus-free stock. In most cases their identity was established by competent entomological specialists.* In two cases, unfortunately, exact identifications were not made. Sprouting tubers were infested as a rule in glass tumblers covered with fine lawn held in place with a strong rubber band. The insects were removed by steeping the tubers in an insecticide. The plants to be infested were always grown in pots in an insect-proof house, and were caged and then usually removed to the laboratory for the purpose of introducing insects to the cages. They were afterwards grown under the cages in pots in the open, or sometimes in insect-proof houses.

Identification of any disease which resulted was made as soon as symptoms of secondary disease developed. The great majority of the plants which gave apparently negative results in the first season, as well as their controls, and in addition many of the plants which gave positive results in the first season, again with their controls, were grown in the open in the following year, when their state of disease or health, respectively, was confirmed. This applies not only to plants grown under cages after infestation, but to many of those grown in the open from tubers, the sprouts of which were infested, in experiments in which the results were apparently negative. In this latter case the plants were dug in July in their first season to minimize chance infection. There is, therefore, no question of leaf-roll being latent, or of faulty diagnosis.

The following table presents a summary of all attempts to infect potatoes through the sprouts or foliage by means of aphides carried out in years 1922 to 1928, with their results.

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* The identifications were made in 1922, 1923, and 1925 by F. W. Theobald, and in 1928 by Kenneth Smith, to whom we are much indebted.

Portion of every tuber used to raise the plants enumerated below was grown as a control, and no leaf-roll developed in any of the resulting plants. For the sake of simplicity also, the experiments, all of which gave negative results, in which various aphides were transferred from healthy plants to healthy plants are also omitted.

Year.	Aphides used.	Stock of aphides raised from	No. of plants or tubers infested.	Variety.	Where grown.	Infestation carried out on	No. of aphides used per plant.	No. of days aphides remained on		No. of plants which		Observations in later season.
								Source of infection.	Healthy plant.	Developed leaf-roll.	Remained healthy.	
1922	Myzus persicae	Colony on potato sprouts	7	—	In open	Sprouts	12–24	Long period	13–52 (+)	4	3	Not grown.
1923	Macrosiphum solanifolii	Colony on rose in winter	3	President	In house	Sprouts	15–18	25	15	0	3	No leaf-roll in 1924.
	do.	Colony on potato sprouts	99	Arran Victory Up-to-Date	In open	do.	Many	14–18	24–35	0	99	29 leaf-roll plants appeared in infested plants in 1924, and 20 in controls, evidently due to contamination in the field.
	do.	do.	48	Kerr's Pink Up-to-Date	do.	do.	42–8	18 (+)	0·7–13 (1)	1	47	Not grown.
	do.	do.	1	British Queen	In house	do.	28	14	26	0	1	No leaf-roll in 1924.
1924	Not identified	Colony on potato sprouts	9	British Queen	In cages	Foliage	25	1-14 (2)	20–2	0	9	No leaf-roll in 1925.
	do.	do.	7	do.	do.	do.	100–8	49	1–3 (3)	0	7	do.
	do.	do.	1	do.	do.	do.	192	49	3	0	1	do.
	do.	do.	10	Arran Chief	In house	Sprouts	Many	—	29	0	10	do.
	do.	do. (4)	6	British Queen	In open	do.	Indefinite	14	23	5	0	Not grown.
1925	Myzus pseudosolani	Single ♀ from loganberry	3	British Queen	In house	Sprouts	24	8-15-22	20–21	1	2	Confirmed in 1926.
	do.	do.	24	do.	In field	do.	40–50	13–28	7–30	1	23	Not grown.
	do.	do.	2	President	In house	do.	50	13	14	0	2	No leaf-roll in 1926.
	do.	Colony from loganberry	6	British Queen	In field	do.	34	35	7	0	6	Not grown.
	do.	do.	4	President	In house	do.	33–50	13	14	0	4	No leaf-roll in 1926.
	do.	do.	1	do.	In cage	Foliage	200	12	27	0	1	No leaf-roll in 1926.
1926	Not identified	Colony on potato sprouts	1	President	In cage	Foliage	200	20	26	0	1	No leaf-roll in 1927.
1928	Myzus persicae	Single ♀	6	Kerr's Pink	In house	Sprouts	20–50	19–30	14–18	15	3	Confirmed in 1929.
			12	do.	In cages	Foliage						

(1) In portion of this experiment the aphides, after having fed on diseased plants for at least 18 days, were transferred from one healthy plant to another, usually at intervals of 24 hours. In the final transfer, the number of insects was reduced to eight, but a much larger number was used on the majority of plants.

(2) The aphides were transferred to healthy from diseased plants at intervals of 1 to 2 days after being first placed on the latter.

(3) Practically the same explanation applies as is given in note (1) above.

(4) Two different lots of aphides were used in 1924.

TABLE II.

SUMMARY OF INFECTION EXPERIMENTS WITH APHIDES (1922–1928).

Aphides used.	No. of plants or tubers. Infested.	Developed leaf-roll.
Myzus persicae	25	19
Myzus pseudosolani	40	2
Macrosiphum solanifolii	151	1
Unidentified aphides	34	5

One result is clear from these experiments—namely, the great preponderance of positive results secured in the two cases in different years in which *Myzus persicae* was used;* and the almost, but not quite, negative results in the more numerous experiments in which other aphides were employed. Many of the latter were tried under apparently the same conditions as *Myzus persicae*. In other experiments factors were varied, such as temperature and lighting during infestation, the length of the stay of insects on diseased and healthy plants, the number of insects transferred, but not to such an extent as to affect the result materially. The age of the plants was varied also, as we at one time suspected that our negative results might be due to using plants at too advanced a stage. As will be shown, however, the age of the healthy plant to be infested, or of that providing the inoculum, is not a barrier to the transference of leaf-roll infection by *Myzus persicae* within the limits used in these experiments, although it is easier to infect young plants. Neither does it matter in the case of this insect whether tubers which have been infested are sprouting in air or are allowed to root in soil, with the sprouts projecting above the surface. It is evident, therefore, that *Myzus persicae* possesses a facility for transmitting leaf-roll which is not shared by the other aphides mentioned. Elze (3) has come to the same conclusion, although his results with the others were more frequently positive than ours.

The case of *Myzus pseudosolani* and *Macrosiphum solanifolii* is not so simple. The positive results are few, but some at least of them were secured under conditions seemingly capable of excluding infection through any other agency. Thus in the first experiment in 1925, one out of three British Queen plants was infected in an insect-proof house by means of *Myzus pseudosolani* raised from a single female. These insects were identified by Theobald. Infestation took place on the sprouts in the laboratory in April, when no other aphides were being worked with, and there was no possibility of other insects being introduced. Unless, therefore, infection took place through the foliage after the plant came up in the house, and this under the circumstances appears to have been impossible, the disease must be attributed to the action of *M. pseudosolani*. This plant developed secondary leaf-roll within twenty-eight days of its appearance above ground, while the control plant derived from the other half of the

* Similar results are now being secured with *Myzus persicae* in 1929.

same tuber showed no leaf-roll then or afterwards. The development of leaf-roll in this form and at such a time is inconsistent with recent infection through the foliage.

It is probable, therefore, that *Myzus pseudosolani*, and possibly *Macrosiphum solanifolii*, are capable of conveying leaf-roll from plant to plant in the case of the potato. This is in general harmony with other work (15, 16, and 3). Since, however, they did so in such a small proportion of the cases tried, it is probable that they are not responsible for an appreciable amount of the naturally occurring infection in the field. If this be so, the distribution of *Myzus persicae* becomes a factor of preponderating importance in the leaf-roll problem.

There remains the question of the conveyance of leaf-roll by means of capsid bugs and jassids (*Typhlocyba* sp.), evidence for which was first presented by one of us (7) in 1923. Supplementary evidence concerning the capsids (*Calocoris bipunctatus*) was given in 1926 (10), and this, though it relates to a single infection secured from three inoculated plants, was carried out in an insect-proof house and does not appear open to question. Further work is desirable, but it is probable that *Calocoris bipunctatus* has the same relationship to leaf-roll as *Myzus pseudosolani* and *Macrosiphum solanifolii*.

Nevertheless, we have reason to modify the views then held as to the practical importance of capsids and jassids. At that time owing to their abundance, and the apparent scarcity of aphides, in a field in which leaf-roll was spreading rapidly, it was believed that they were the principal agents responsible. Time has not confirmed this view. *Typhlocyba* has never been seen in any numbers in potato fields since 1921, and it can be no factor in the situation. *Calocoris* is more or less abundant every year, particularly around the edges of fields near the hedges; but a field experiment has shown that healthy potatoes grown in the same drill as plants affected with leaf-roll, on all of which it fed to such an extent as to injure them severely, produced a crop which was entirely free from this disease.

Experience has also tended to confirm the relationship between the appearance of leaf-roll in the field and the occurrence of aphides. The former follows the latter, and the disease spreads most during the aphis season in June and July. Furthermore it is now evident that a very small number of certain aphides is capable of initiating a considerable amount of new infection. The disease has been experimentally transmitted by us by means of a single individual of the species *Myzus persicae*.

It follows from this that leaf-roll is probably not one of these virus diseases restricted for its distribution to a single insect. On the other hand, it appears that, while theoretically it is capable of being carried by a number of living agents, practically one agent is largely responsible for its spread.

It would appear, therefore, that the problem of discovering the agents of dispersal of leaf-roll has been largely solved. The mosaic problem, however, is a different one; and while more work is needed it is possible to say that *Myzus persicae* has not the same importance for this disease as it has for leaf-roll.

Conditions under which Myzus persicae *transmits Leaf-roll.*

The conditions under which *Myzus persicae* can infect plants with leaf-roll were studied more thoroughly in 1928–1929, with particular reference to the age of the plant, the time the first symptoms appear, and the form they assume. It was sought to convey infection (1) from the sprouts of unplanted tubers to (*a*) similar sprouts, (*b*) young plants; (2) from young plants to (*a*) young plants, (*b*) full-grown plants; and (3) from full-grown plants to (*a*) young plants, (*b*) full-grown plants. The young plants were, when used, 7·5 to 23 cm. high and had been planted 13 to 22 days; the full-grown plants were 70 to 75 cm. high and had been planted 53 to 107 days, depending on the season. As all plants were grown under glass, where growth is rapid, about one month should be added to these periods to approximate to the corresponding state of growth out of doors. Plants would reach approximately the same sizes in the field at the end of May and early in July.

The aphides used were derived from a single ♀ and their original health was proved by infesting healthy plants. These remained free from virus infection in 1928 and 1929. The aphides were then placed on a plant affected with leaf-roll and left there for periods varying from 19 to 30 days before being used. The latter plant was also grown, to show that the desired disease was present. The healthy plants (variety Kerr's Pink), each with an individual tuber control, were grown throughout in insect-proof houses. The plants, the foliage of which was to be infested, were covered with muslin cages during the period of infestation, while their controls were not so covered; nor were the plants from tubers infested on the sprouts before planting. The aphides were used at the rate of 20 to 50 per plant and remained on the healthy infested plants, or sprouts, for 14 to 18 days. The results of the experiment are shown in the following table:–

TABLE III.

AGE OF POTATO PLANTS IN RELATION TO INFECTION WITH LEAF-ROLL THROUGH THE AGENCY OF *Myzus persicae*.

Age of source of infection.	Infested plants. Age (days after planting).	No.	Days from beginning of infestation to development of definite symptoms.	Nature of first symptoms in first season.	No. of plants which showed leaf-roll during first season.	Result in following season.	No. of original plants finally infected.
Sprouts	Sprouts	3	32	Secondary LR; no primary.	3	4 plants: 4 LR. 6 do. : 6 LR. 12 do. : 12 LR.	3/3
do.	Young plants (13 days)	3	38	Primary LR, passing into secondary.	3	10 plants: 10 LR. 12 do. : 12 LR. 8 do. : 8 LR.	3/3
Young plants	Young plants (22 days)	3	31–43	Primary LR, passing into secondary.	3	12 plants: 12 LR. 11 do. : 11 LR. 8 do. : 8 LR.	3/3
do.	Full-grown plants (53 days)	3	40–60	Primary LR; no secondary.	3 (PLR)	12 plants: 12 LR. 9 do. : 9 LR. 11 do. : 11 LR.	3/3
Full-grown plants	Young plants (15 days)	3	54	Primary LR, passing into secondary.	2	7 plants: 7 LR. 7 do. : 4 LR, 3 H. 17 do. : 0 LR, 17 H. (1)	2/3
do.	Full-grown plants (81 days)	3	Over winter	None.	0	11 plants: 7 LR, 4 H. 12 do. : 0 LR, 12 H. 12 do. : 0 LR, 12 H.	1/3
Control plants (2)		18	—	—	0	72 plants: all healthy.	0/18

(1) The aphides did not thrive on this plant in 1928.
(2) Derived from half of each tuber which produced plants listed above.

Examination of the table will show that infection was conveyed under all the conditions tried. Symptoms of disease developed more rapidly, the younger the inoculated plant and the more rapid its growth, and apparently also the younger the plant providing the infection. When infection was conveyed to young plants from sprouts, young plants, and full-grown plants, respectively, the corresponding intervals elapsing before definite leaf-roll appeared were 38 days, 31 to 43 days, and 54 days. This is apparently correlated with greater ease of infection when both plants are young. Compare Elze's (3) Table XIII in this connection. On the criterion of the incubation period (if such a term may be employed in this connection), transference of

infection is likely to be most easily accomplished in the earlier stages of growth.

Confirmation of this is found in an apparent increase in the difficulty of bringing about infection (at least of the tubers) in the last two experiments. This may be seen from the fact that some of the plants in question produced both diseased and healthy tubers ("mixed units"), while only one produced nothing but diseased tubers. The comparative failure to infect depends in part on the age of the source of disease, seeing that three of the inoculated plants were young and three full-grown. Infection is rendered most difficult, however, when both the source and the inoculated plant are old. Elze (3) has shown that when plants are infested during the last weeks of growth, no leaf-roll infection reaches the tubers.

There are probably two explanations of the occurrence of "mixed units," that is the production of both diseased and healthy tubers and plants by the same individual, when disease is contracted comparatively late in the previous season. One arises from the difficulty of bringing about infection at this stage of growth. The decay of the mother tuber also has an influence, for this destroys the continuity of the tubers produced on separate stalks of the same plant. In reality, all the shoots produced by a seed-piece constitute separate plants once the latter decays.

The first symptoms developed following infection at different stages of growth present points of much interest. These symptoms depend entirely on the age of the inoculated plant, and not on the character of the source. Infection of the sprouts of unplanted tubers results in the development of secondary leaf-roll very early in the season, usually without the intervention of the primary stage, as we (7) have already pointed out. The result is hardly distinguishable from that secured from tubers produced by plants affected in the previous season, and the two should not be confused. The time at which the disease was contracted can be easily determined by planting, as a control, portion of a tuber, on the other portion of which viriferous insects are placed in spring. If no pre-seasonal infection is present the control remains healthy, while the infested tuber-portion produces a plant showing secondary leaf-roll early in June. The plants can be grown in the open, at least at Glasnevin, and the results secured with perfect safety in the earlier portion of June, before there is any seasonal spread of infection. Even when the latter appears, it always begins as distinct primary leaf-roll. We have followed this procedure for a number of years on a large scale as a supplement to work under glass, using the core-grafting method of tuber infection with various mosaic diseases (10), with complete success. The same is the case elsewhere (1). Unfortunately core-grafting is not applicable to leaf-roll, but an equally certain substitute is now available.

As will be seen by further reference to Table III, infection of the foliage of young plants from whatever source results in the development of primary leaf-roll, more or less rapidly passing into secondary. The younger the infected plant and the more rapid its growth, the more quickly secondary symptoms appear. The two stages frequently occur together on the same plant. This is

sometimes seen in the field, and is associated there also with infections which appear very early (end of June to early July). Sometimes the transition to secondary leaf-roll is rapid, but the time of infection is never in doubt if the plants are frequently inspected. The effect on the yield in such cases is considerable.

When plants are not infected until nearly full-grown (53 days after planting in the experiment under glass, corresponding approximately to 83 days in the open, or usually about the first week of July), primary leaf-roll alone appears, and there is no further development during the same season. This is borne out by field experience. When infected at a somewhat later stage (81 days after planting in the experiment, corresponding approximately to the stage reached in the field about August 1st) no symptoms develop in the season in which infection takes place.

It will be seen that it is possible to tell with considerable accuracy the time at which a plant becomes infected with leaf-roll in the field by knowledge of the time at which symptoms first appear, the nature of the symptoms, and the character of the resulting crop in the succeeding year. Infection through the sprouts before planting results in secondary leaf-roll developing soon after the shoots appear above the ground (first half of June). Early field infection through the foliage is marked by the early appearance of primary symptoms (July) which may become secondary in the same season. In both these cases the crop is usually totally diseased. Later infections may produce primary leaf-roll in the same season, or on the other hand the infected plants may not be altered in outward appearance. A proportion of the tubers remains healthy, as a rule, thus resulting in "mixed units." It should be noted that the same result may follow from sprout infections. The first reaction after infection is also influenced by the variety, some varieties, such as President and Lochar, showing primary symptoms more readily than others.

Summary.

The literature of the subject is reviewed, and a list is given of the insects found by various workers to be capable of conveying leaf-roll, both aerially and through the soil. The difficulties which have been experienced in experimental transmission, and in correlating field outbreaks with aphides, are referred to.

In experimental work with aphides extending from 1922 to 1928, the number of successful leaf-roll infections secured with *Myzus persicae* were 19 out of 25; with *Myzus pseudosolani*, 2 out of 40; with *Macrosiphum solanifolii*, 1 out of 151; and with unidentified aphides, 5 out of 34.

Myzus persicae possesses a facility for transmitting leaf-roll which is not shared by the other aphides mentioned.

Reasons are given for believing, in spite of the few positive results secured, that *Myzus pseudosolani* and *Macrosiphum solanifolii* have the power of transmitting infection, at least occasionally. The same is believed to be true of *Calocoris bipunctatus*.

Leaf-roll is probably not one of the virus diseases restricted to a single insect vector.

Observation shows that insects other than aphides play no appreciable part in causing infection in the field. The part played by *Myzus persicae* is believed to be a predominant one, and it is probably a factor governing the distribution of leaf-roll. This insect does not appear to have the same significance for the mosaic diseases of the potato.

Myzus persicae is capable of conveying infection from sprouting tubers, young plants, or full-grown plants to sprouting tubers, young plants and full-grown plants.

The younger the inoculated plant, and apparently also the younger the plant providing infection, the quicker the symptoms develop on the former. This is correlated with greater ease of infection in the earlier stages of growth. When either or both the inoculated plant and the source of infection are old, infection at least of the tubers is rendered more difficult.

The first symptoms which develop following infection vary with the age of the inoculated plant. Infection of (1) sprouts, (2) young plants, (3) plants of medium age, and (4) older plants, results respectively in (1) secondary leaf-roll, (2) primary leaf-roll passing into secondary, (3) primary leaf-roll persisting for the season, and (4) no symptoms during the same season.

Plants infected early in the season generally give rise to a totally diseased crop in the following year. The tubers of those inoculated late in the season may escape infection altogether, or some of them may become diseased and some remain healthy.

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No. 28.

THE PHOTO-CHEMICAL AND PHOTO-ELECTRIC MEASUREMENT OF THE RADIATION FROM A MERCURY VAPOUR LAMP.

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AND

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Introduction.

Among the sources of ultra-violet light, the quartz mercury vapour arc lamp has come to be largely used. It is well known that its potency in its action on the skin, with the production of erythema, decreases with time. Measurements were begun about a year ago to examine the behaviour of a Hewettic Levick Ulviarc Medical Lamp, air cooled type, in the Plymouth Department of Public Health at Stonehouse. This is designed to work at 230 volts, taking 3½ amperes, but as the Plymouth voltage is only 210 volts the current is probably rather less. We are indebted to the Medical Officer of Health, Dr. A. T. Nankivell, D.P.H., and to Miss M. Smellie, M.B., D.P.H., for extending to us every facility in its use, and we are further indebted to Dr. Smellie for assistance in many of the measurements.

Photo-chemical Measurement.

The method of chemical examination adopted was the decomposition of uranyl oxalate, as described by us in an accompanying paper (1929, 2). The mechanism of the reaction has been studied in great detail by Büchi (1924), to whose work reference may also be made for the literature.

A few experiments were also made using Webster, Hill, and Eidinow's (1924) acetone methylene blue solution, and the nitrite test described by Gillam and Morton (1927, 1928). The interesting results obtained by the latter only became available after our own work had been in progress for about six months, otherwise simultaneous tests would have been carried out by the nitrite method also. According to their results the lamp fell to 50 per cent. of its initial radiation in about 230 hours, as indicated by the oxalate method, and to about 28 per cent., according to the nitrite production test. The oxalate and methylene blue methods agreed well; the latter, however, gave slightly lower results. The differences are due to the fact that these two methods are sensitive to longer wave-lengths than is the nitrite method: the deposit on the tube, therefore, affects the latter to a greater extent; another cause is mentioned later.

According to Büchi the oxalate method is sensitive well into the blue region; Anderson and Robinson (1925) state that all below 3600 Å.U. is absorbed with 25 mm. thickness of solution, and that at 4100 Å.U. there is partial absorption with 0·1 *N* oxalic acid which is also 0·01 *M* with respect to uranyl sulphate.

Our exposures were made with the concentrations given by Anderson and Robinson, who, however, used 4·27 g. uranyl sulphate, $UO_2SO_4.3H_2O$ per litre, not 4·203 g., which is 0·01 *M*; no reason was given for this difference, but before we noticed it we started with 4·27 g., and have continued with that concentration. The mixture must be stored in the dark. Quartz tubes, 13 × 1·6 cm. (internal diameter 1·3 cm.) were used, each containing 10·0 c.c.; the amount of unused oxalic acid was determined, after exposure, by titration with 0·1 *N* permanganate. The tubes were placed, uncorked, at an angle of 15° with the horizontal, at a distance of two feet (61 cm.) from the lamp, the long axis of each being parallel to the long axis of the lamp.

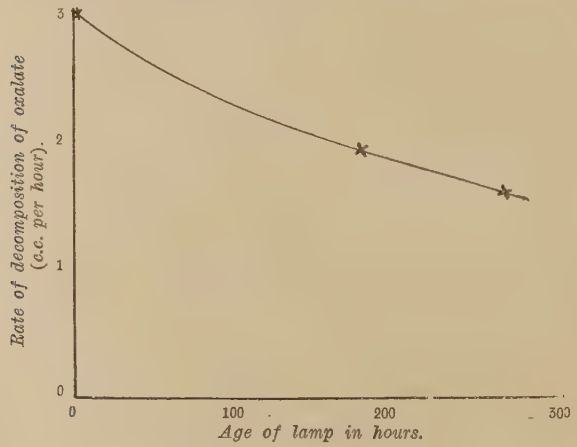

Fig. 1.

Since, however, some of the visible and all the longer ultra-violet radiation is effective in decomposing the oxalate, it appeared that a truer index of its therapeutic value could be obtained by carrying out simultaneous exposures with tubes both unscreened and screened by a plate of glass known to cut off all rays of anti-rachitic value. For this purpose a sheet of unpolished Pyrex glass, 4·0 mm. thick, was used (Luce, 1926). The Corning Glass Company's filter Corex A, which, in 4·98 mm. thickness, transmits to 2400 Å.U., and has 80 per cent. transmission at 3000, was also used, but, this sheet being 8·6 mm. thick, the transmission was somewhat reduced. It, however, transmitted freely to 2500 Å.U. as judged by a Beck fluorescent screen spectroscope. A test tube of Monax resistance glass was also used, the dimensions being similar to those of the quartz.

TABLE 1.

To show rate of destruction of oxalic acid in uranyl oxalate solution when exposed to Hewittic Levick mercury vapour arc, with reflector. Tubes placed with long axes parallel to long axis of lamp at 2 ft. (61 cm.) from its centre. Asterisk denotes tubes placed perpendicular to axis of lamp, distance measured to middle of solution. Lamp run 8–9 hours a week, which may be taken as 1·2 hrs. a day—the tabulated number of hours in use is based on this figure.

Date.	Lamp.	Hours. in use.	Rate of destruction (unscreened). c.c. per hour.	Rate of destruction (unscreened). Percentage.	Screen.	Transmission of screen per cent.	Anti-rachitic (and reflection losses) per cent.
27/ 6/'28.	No. 1, old	—	1·12	38	—	—	—
2/ 7/'28.	No. 2	3	2·94	100	—	—	—
16/11/'28.	„	165	1·62*	55*	Pyrex	40	60
„	„	165	1·62*	55*	Corex, clear	70	—
26/11/'28.	„	177	1·87	64	—	—	—
6/ 2/'29.	„	266	1·56	53	Pyrex	37	63
„	„	266	1·56	53	Monax	46	—

Table 1 shows the rate of deterioration of the lamp. Based on the rate of destruction of the 0·1 *N* oxalic acid mixture, as given in column four, percentages are tabulated in column five. The rate of reaction was reduced by the interposition of the screens shown in column six; the ratio of the screened to the unscreened rate is given in column seven as the percentage transmission. The thicknesses of the screens were:—Pyrex 4·0 mm., Corex clear, 8·2 mm., Monax—not a screen, but a test tube of same dimensions as the quartz tubes used, with wall 0·9–1·1 mm. thick.

The column headed "Anti-rachitic (and reflection losses)" shows the difference between the transmission of the Pyrex and the unscreened value. It may be taken as giving as near a measure as we can get to the true anti-rachitic value of the lamp, because it has been shown by Luce (1926) that even 2 mm. of Pyrex cuts off all the anti-rachitic portion of the spectrum, or at least that rats exposed to full sunlight through Pyrex develop rickets. There are of course certain corrections to be applied, viz., the Pyrex transmission is too low by 4 per cent. of the incident light reflected from its front surface, and by 4 per cent. of what gets through reflected from its inner surface (glass-air), viz., the total loss is approximately 6 per cent. of the incident light. Secondly, the Pyrex, though it cuts off fairly sharply, does undoubtedly screen out some radiation of no anti-rachitic value; this also tends to make its transmission too low. To sum up, of the principal lines of the mercury arc spectrum, it transmits 5460 Å.U., which has little, if any, effect upon uranyl oxalate; it transmits

4360 and 4050, both of which act on the oxalate; its transmission of 3650 is probably somewhat reduced; it cuts out altogether the 3130 and 2600 Å.U. lines, both of which are anti-rachitic, especially the 3130 line. The transmission of the Pyrex is, accordingly, too low by 6 per cent. for reflection loss and, probably, by a few per cent. more, owing to the cutting out of non-anti-rachitic radiation. The value tabulated is therefore probably about 10 per cent. higher than the true anti-rachitic value of the light, which would, accordingly, be not much over 50 per cent.

The deterioration of the lamp is due, according to Gillam and Morton, to a non-selective loss in transmission, arising from the deposition of a film of silicon, following upon a shortening of the spectrum in the extreme ultra-violet, occasioned possibly by the formation of silicon monoxide vapour inside the lamp. Our results bear out the view that the loss is non-selective, as the proportion screened out by the Pyrex glass showed no diminution between 165 and 266 hours of use of the lamp. The Pyrex screens out almost all the radiation responsible for the nitrate ——> nitrite reaction, as shown by the facts that, with Pyrex screens, 20 min. exposure of nitrate solution in quartz tubes at 50 cm. distance from the old lamp gave no trace of nitrite, and 15 min. exposure to the new lamp gave only a faint trace of nitrite, about 2×10^{-6} mg. nitrite nitrogen in the 10 c.c. tube. The unscreened tubes gave relatively very large amounts, in the ratio of 100 : 42 for the new lamp and the old one after 360 hours' use.

The transmission of red purple Corex A, 3 mm., was found by Luce to be adequate to protect rats against rickets when exposed to full sunlight. It is opaque to visible light beyond 4250 Å.U., and shows transmission to 2650 Å.U. with 77 per cent. at 3000 Å.U.[1] An unpolished sheet 10·2 mm. thick was calculated from data supplied by the Corning Glass Co. to transmit 0·00 per cent. at 4000, 42·5 per cent. at 3400, 15 per cent. at 3000, and 0·7 per cent. at 2800 Å.U. Used as a screen with the mercury vapour arc and oxalate mixture its transmission was ascertained to be 19 per cent. Though it cuts out the region of maximum erythema production, 2970 Å.U. (Hausser and Vahle, 1922), its transmission is probably the best suited for measuring the effective portion of sunlight, since sunlight is deprived of these shorter waves by the atmosphere, and the oxalate mixture is sensitive to longer waves of no ascertained anti-rachitic or erythema-producing potency.

We have not used Hill's test systematically with the lamp, but it was found that upon a certain date an exposure of one hour was equivalent to about 5 methylene blue units; therefore one methylene blue unit, namely, 2–4 erythema units, was equivalent to 12 minutes' exposure to this lamp, the distance being two feet. Erythema should, therefore, be produced in from 3–6 minutes,

[1] Quoted from Luce (1926). The data given further on in this paper are taken from a curve supplied by the Corning Glass Co.

according to the sensitiveness of the skin of the person tested. Exposures were, accordingly, made of the front of the left biceps, the arm resting on the 2 ft. line, the skin being about 4 inches nearer, viz., at 50 cm. Exposures of 3, 4½, and 6 minutes were made; two hours later all three showed erythema, the intensity being clearly in the order of time of exposure. After 5½ hours no very marked difference could be noted between the irradiated areas, but the three minutes' exposure showed slightly less intense erythema. On pressing the areas momentarily with the ball of the right third finger the true order became at once apparent: namely, the 3-minute exposure blanched readily, the 5½-minute blanched slightly, and the 6-minute did not blanch, unless heavier pressure were applied. The exposures had been made at 5 p.m. on a Monday, at 10 a.m. On Tuesday the 3-minute exposure could still be distinguished from the others, and on Wednesday it was much lighter. It subsequently faded, leaving little pigmentation; the other exposures were still red four days later, and left a marked pigmentation. It seems, therefore, that at an actual distance of 60 cm., instead of 50 cm., 3 minutes' exposure, or even slightly less, would be the time required to produce a slight degree of erythema. This corresponded, on the date of the experiment, with the destruction of 1·87 c.c. of 0·1 *N* oxalic acid or 11·8 mg. of oxalic acid per hour, viz., 0·59 mg. per 3 minutes. Since the internal diameter of the tube was 1·3 cm. and the length of the liquid column in it approximately 8 cm. in its sloping position, the effective area of the tube with respect to the linear light source is accordingly this length multiplied by the diameter, viz., 10·4 sq. cm. The erythema dose corresponds approximately, therefore, to the decomposition of 0·056 mg. oxalic acid per sq. cm. when the mercury arc is the source of radiation. The figure is probably rather too low, as absorption could not have been nearly complete at the edge of the tube, also reflection losses must be considerable. The subject was a light-skinned adult, not given to much pigmentation.

Photo-Electric Examination of the Mercury Vapour Arc Lamp.

We have previously described the use of the Burt vacuum sodium photo-electric cell for daylight photometry (1929). Fig. 2 shows the arrangement used by us, in which, on the left-hand side, the cell is shown connected to a universal shunt and a Tinsley portable galvanometer, giving 12·5 scale divisions per micro-ampere. Readings can be estimated to 0·1 scale division, viz., to 0.008 μa. The Onwood micro-ammeter shown on the right of fig. 2 would, however, have been sufficiently sensitive for this work. It seemed probable that this outfit would serve to give a good indication of the behaviour of the mercury vapour arc, since the maximum sensitivity of sodium is close to 3620 Å.U., and the thin soda glass of the bulb of the cell is transparent down to 3200 to 3300 Å.U., or even further, on account of its thinness. Dr. Burt prepares sodium photo-electric cells of quartz specially for testing sources of ultra-violet light. The spectral sensitivity curve for sodium shows that, for a uniform

spectral energy distribution, 50 per cent. of the reading of such a cell is due to wave-lengths between 3620 and 4800 Å.U., 32·6 per cent. to the range 3000 to 3620, and 17·4 per cent. to that from 2000 to 3000. But owing to their smaller size these quartz cells are necessarily less sensitive than the glass cells, and the cost is five times as great; moreover, since the photo-chemical results have shown a fairly close correspondence between the rate of depreciation in the longer and the shorter wave-lengths—except for

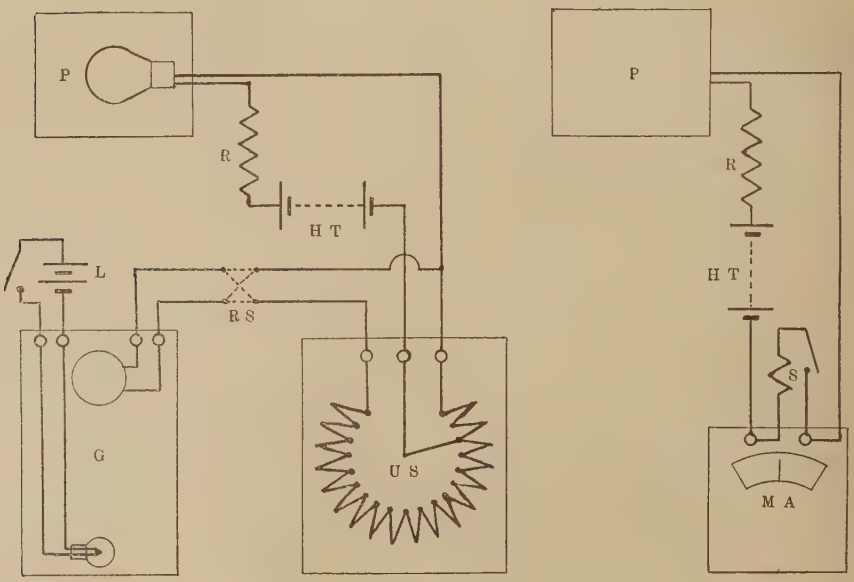

Fig. 2.

L, galvanometer lamp battery. G, portable mirror galvanometer. RS, reversing switch. US, universal shunt. HT, high tension batteries, 60 volts. R, safety resistances, 10,000 ohms. P, photometers, the photo-electric cell is indicated in that on the left. MA, Onwood micro-ammeter. S, shunt, to one-fifth. For standardisation of G, the P circuit was removed, and MA, with dry cell, connected to US instead. For comparison of the three photometers they were connected, in quick succession, to US, but only one is shown in figure.

the extreme ultra-violet—the glass sodium cell should indicate correctly the behaviour of the lamp for therapeutic purposes. It should be borne in mind that, though the very short wave-lengths of the mercury vapour arc 2100 to 2700 Å.U. are active in producing erythema, and, consequently, are of therapeutic value as irritative agents, yet the region of maximum potency is about 2970 Å.U., according to the results of Hausser and Vahle (1922), decreasing to

zero at 3150 Å.U. It would seem, then, that the use of the glass sodium cell as a means of testing the ageing of the lamp should be legitimate. Tests were made with the opalized surface of the photometer at a distance of 50 cm. from the middle of the quartz tube of the lamp, the surface being perpendicular to the light. Two lamps were tested, one of which had been in use for 10 months, the other being quite new at the commencement of the tests. Exposures were made both with and without the opalized diffusing surface. Two screens were also tested—one a sheet of unpolished Pyrex 4·0 mm. thick, and the other of red purple Corex A glass, unpolished, 10·2 mm. thick. The transmission curve for a screen of this glass 2 mm. thick shows that it has a maximum transmission factor, 79 per cent. at 3400 Å.U., and transmits 35 per cent. at 2800 and also at 3880, and only 5 per cent. at 4000. From these figures we find, allowing for a reflection loss of 8 per cent. at the two surfaces, that our screen should transmit 42·5 per cent. at 3400, 0·7 at 2800 and at 3880, and only 0·00003 per cent. at 4000. This screen transmits scarcely any visible light, but, as will be seen from Table 2, it transmits a considerable percentage of the total radiation measured by the sodium cell.

TABLE 2.

Transmission of various glasses for the radiation of the mercury vapour arc as measured by the Burt glass cell, maximum sensitivity near 3600 Å.U. probably. Glasses used one at a time:—double surface flashed opal glass, 1·8 mm. thick; red purple Corex A, 10·2 mm.; Pyrex, 4·0 mm.—this cuts off all the anti-rachitic radiation sharply.

Lamp.	No screen.	Opal.	Red purple Corex A.	Pyrex.	*Anti-rachitic (and reflection losses).
New, April 25th ...	100	—	32·3	75·0	25·0
New, April 26th ...	100	45·8	33·5	73·3	26·7
Old, April 26th ...	100	47·5	29·8	75·1	24·9

* But see the qualifying remarks concerning use of Pyrex screen in Table 1.

Another point which has to be taken into consideration is that the radiation from a mercury arc does not assume a constant value for some time after the arc is struck, as has been shown by D. T. Harris (1929), using a Griffiths cadmium photo-electric cell with a quartz window, and a single valve amplifier. The arc we used gives a moderate value when started, which after a minute has decreased to about one-half. It is, however, impossible to measure the current the instant the lamp starts to glow. The decrease is followed by a rise, which, when the lamp was fitted with a stainless steel reflector, reached a maximum value about 15 times as great as the minimum, after which there was a slight fall to the final steady state. With a lamp not provided with a reflector Harris found that, in still air, the steady state was reached in about the same time (5 minutes) without the occurrence of the intervening maximum. The results

plotted in fig. 3 show that these changes can be studied by means of the sodium cell without the use of an amplifier.

We desire to express our thanks to the Government Grant Committee of the Royal Society for enabling us to purchase the photo-electric cells, also to Dr. F. G. Bushnell, for the loan of the acetone methylene blue standards.

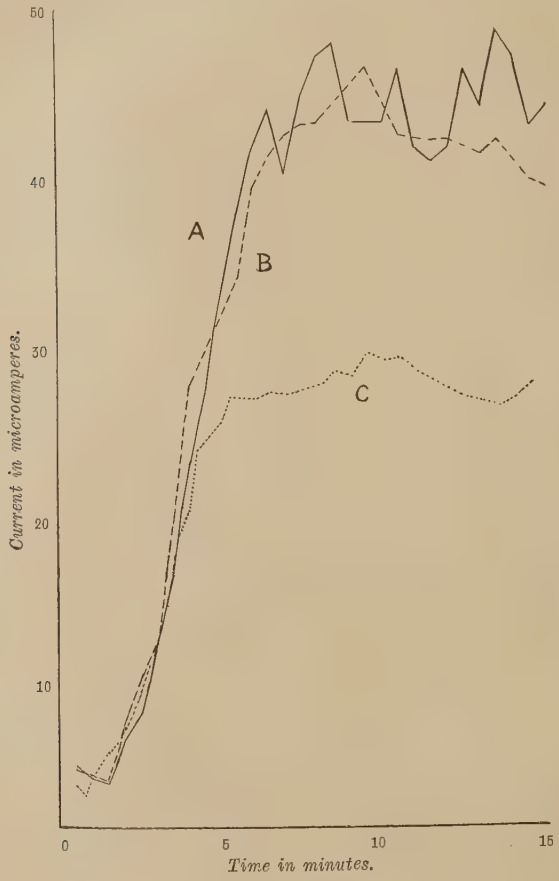

FIG. 3.

SUMMARY.

1. The uranyl oxalate method was used to study the rate of deterioration of a quartz mercury arc. The decrease in radiation appears to be non-selective, or nearly so, for the visible portion and near ultra-violet as compared with the middle and far ultra-violet stopped by 4·0 mm. of Pyrex glass. The Pyrex

transmitted 40 per cent., clear Corex A (8·2 mm.) 70 per cent., and red purple Corex A (10·2 mm.) 19 per cent.

2. Radiation from a mercury arc produces erythema on the skin of the upper arm when it suffices to decompose roughly 0·056 mg. of crystalline oxalic acid per sq. cm. in 3 minutes, exposure of the uranyl oxalate solution being made in 10 c.c. portions in 13 × 1·6 cm. quartz tubes, internal diameter 1·3 cm., the tubes being placed with long axis parallel to long axis of lamp and at about 15° with a horizontal plane.

3. Changes in a mercury arc may be followed with a glass vacuum sodium photo-electric cell of the Burt type. The 4 mm. Pyrex sheet transmitted enough radiation to produce a current 75 per cent. of that with unscreened cell; that passing the red purple Corex A (10·2 mm.) gave 33 per cent. with a new lamp and 30 per cent. with one which had been in use for 360 hours. Double surface flashed opal glass, 1·8 mm. thick, cut down the current to 46–47 per cent. of the value for the unscreened cell. Owing to the fact that the photo-electric cell is not equally sensitive to light of different wave-lengths these figures are not percentages of the energy transmitted.

4. When first switched on the radiation from the mercury arc falls to about one-half of its initial value within a little over a minute. It then increases rapidly, reaching a maximum approximately fifteen times the minimum value within about 5 or 6 minutes from the start.

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No. 29.

STUDIES ON PEAT.
PART 3: LOW TEMPERATURE CARBONIZATION OF PEAT.

By JAMES T. DONNELLY
AND
JOSEPH REILLY.

[Read November 26, 1929. Published separately February 8, 1930.]

As far as the authors are aware, no recent work has been carried out on the low temperature distillation of peat comparable with that on various types of coal, particularly from the point of view of examination of the tars.

Two samples of peat from the district of Mileen, Co. Cork, were subjected to low temperature distillation at 550° C., as described later, and the resulting tars examined by the method of selective solvent extraction. Under the mild conditions employed during the distillations, exceptionally high yields of tar were recorded, much higher than those usually given in the literature for straight distillations of peat.

Preparatory to distillation, the peat was air dried in the sod condition for two weeks, the sods then being crushed and air drying continued for one week. The peat was then crushed to pass a sieve of twenty meshes to the square inch, and stored in sealed jars. The black peat was entirely free from fibrous matter, and in appearance resembled a black soil. The brown sample was of a fibrous nature. Proximate and ultimate analyses of both samples were made, the results being given in Table I. The calorific values are also given.

Table I.

Proximate Analyses.

Condition of sample.		Moisture.	Volatile Matter.	Fixed Carbon.	Ash.
Brown Peat	air-dried	11.46	42·73	24·10	21·71
	anhydrous		48·26	27·22	24·52
Black Peat	air-dried	11·00	48·06	23·04	17·90
	anhydrous		53·99	25·91	20·10

Ultimate Analyses.

	Ash.	Sulphur.	Nitrogen.	Hydrogen,	Carbon.	Oxygen.	Calorific Value (air-dried peat). Calories.	B.t.u.
Brown	24·52	0·26	2·01	6·84	42·90	23·47	3872	6970
Black	20·10	0·26	1·68	4·95	40·55	32·46	3878	6980

Experimental Work.

Distillation of the peat was carried out in a current of coal-gas in an electrically heated retort. The retort, described below, was so constructed that carbonization was effected by hot gases rather than by direct contact with the heat source. By sweeping off the products of distillation as they were evolved, cracking of the primary tar was prevented. The coal-gas used was obtained

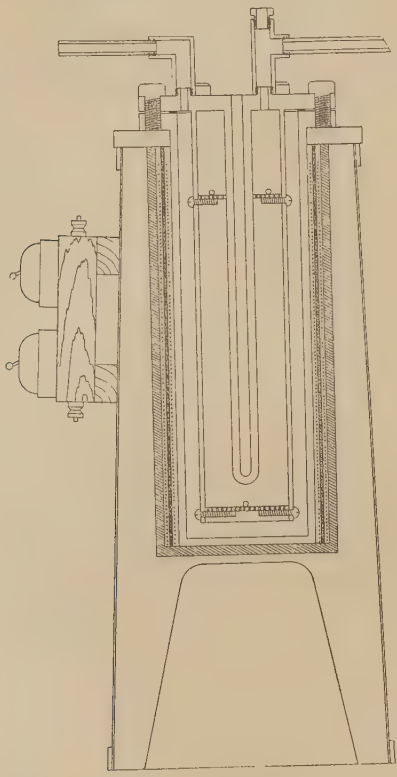


Fig. 1.

from the ordinary laboratory gas main, and was scrubbed successively with concentrated sodium hydroxide solution, concentrated sulphuric acid, concentrated sodium hydroxide solution, and finally dried through calcium chloride and phosphorus pentoxide. A specially devised circulating pump (J.S.C.I., 1927, **46**, 437 T.) was used for pumping the gas. Between the pump and the retort a paraffin gauge was inserted to enable the pressure in the distillation area to be observed.

The retort used in this work was kindly supplied by the Sensible Heat Distillation, Ltd., London, but was modified by the authors, the electrical winding being performed in the electrical workshop of University College, Cork, by Mr. J. M'Kenna.

It consisted (fig. 1) of an inner cylindrical container fitting into an outer closed cylindrical jacket, and leaving an annular space of 1/2 inch between the two. The outer jacket was heated by means of an electrical winding, and gave temperatures up to 650° C. This jacket was permanently fixed into a tripod iron casing. The inner container was welded on to a horizontal flange, which could be bolted down to a similar flange welded to the electrically heated jacket; a gas-tight connection was made with an asbestos washer between the two flanges; a gas inlet was drilled in the upper flange so that the gas could pass into the annular space between the two cylinders, through the centre

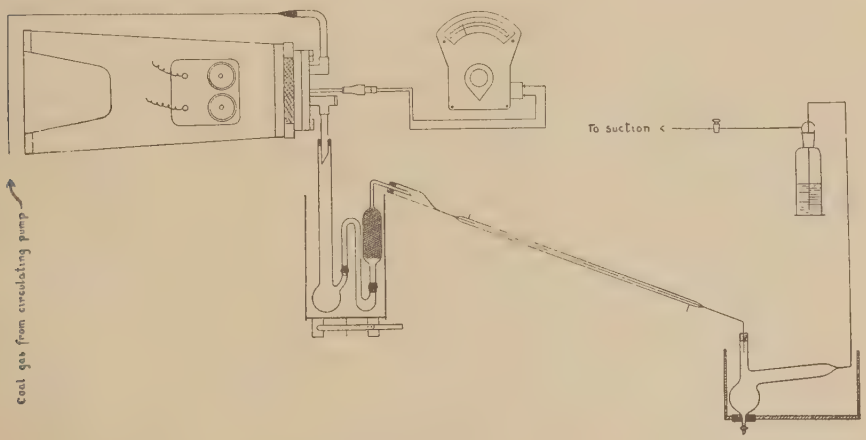


FIG. 2.

cylinder containing the peat, and gain exit through a second aperture drilled in the upper flange. The centre of this flange was drilled and fitted with a closed iron tube for holding a thermo-couple, and the inner container fitted with two perforated iron discs, one at the top and one near the bottom. The peat was kept in position by the perforated discs, the lower one being removed for charging purposes. For a distillation a charge of 500 g. of peat was used, the retort being placed in a horizontal position (fig. 2).

The collection of the liquid products resulting from the distillation of either peat or coal is not one of simple condensation, owing to the presence of a "tar fog." This fog consists of minute vesicles of gas, which are covered with a film of tar. The surface tension effect of the tar surrounding these particles prevents the tar condensing in the ordinary way. In large scale

practice condensation of this fog is effected by Cottrell precipitators or by towers filled with baffle plates, but for small scale laboratory work these types of precipitators are not generally applicable. During some distillation work which the authors carried out on small samples of coal, it was found that passing the vapours through a column of tightly packed glass wool effectively broke the fog and allowed the tar to condense. An advantage of using this method of trapping the fog was that the tube containing the glass wool could be completely freed from the condensed tar by washing with hot solvent.

In carrying out quantitative distillation work it is necessary, for complete extraction of the tar, to use condensing systems which are not complicated. In the present work the tar is collected completely in two condensers.

The first condenser was constructed in three sections, consisting of a long-necked (12 in.), round-bottomed flask, a narrow arm leading from the flask in the form of a double U, and a specially constructed fog-trap, tightly packed with glass wool. The three parts were connected in order with wired-on rubber tubing. The first U in the lead-off arm from the flask acted as a preliminary baffle for the "tar fog," while the second, enlarged to a boat shape, served as a well for condensed tar from the fog-trap. Immersion of this condenser in a bath of calcium chloride solution boiling at 120° ensured that water and oil with boiling points up to 120° were driven over to a second condenser.

The fog-trap consisted of three vertical large-bore glass tubes, connected together at the base and fitted with separate delivery tubes at the top. One of these is seen in the figure, the other two being immediately behind it in the same vertical plane. Any one of the three limbs can be used, the delivery tubes not in use being sealed by insertion in corks fitted into test tubes.

To enable the tar water to be easily separated from the oil, the second condenser was constructed as a flask-shaped separating funnel, with a wide side arm, 8 in. long, leading from the flask at a slight slope. This condenser was immersed in a freezing mixture of ice and salt at $-20°$. In practice it was found that ice was never formed in the outlet arm at a distance of greater than 3 in. from the flask.

Connecting these two main condensers was a water jacketed glass tube, 1/4 in. diameter and thirty inches long, the diameter of the jacket being 1/2 in. This condensing tube was necessary on account of the large amount of steam evolved during a peat distillation. On draining the water from the jacket at the end of a distillation, the centre tube was quickly heated by the hot gas from the retort, and any oil that remained was quickly removed.

During some of the distillation experiments a weighed tube packed with cotton wool was placed after the second condenser, but it was found that it never increased in weight by more than 0·5 g., and that there was no colouration of the wool on exposure to air. This increase in weight was probably due to moisture, and was neglected. As the estimation of ammonia evolved during peat distillations was an important one, a wash bottle containing standard sulphuric acid was placed between the second condenser and the suction to

trap any ammonia that escaped from the second condenser. The ammonia recovered in this way was usually equivalent to 5 c.c. N/10 sulphuric acid.

To overcome the resistance offered by the glass wool to the gas brought by the circulating pump from the main, suction was applied to the end of the condensing system. By means of a fine adjustment tap the pressure in the distillation area was maintained at atmospheric, the tap being opened or closed to the suction as the gas yield increased or decreased.

When starting a distillation one arm of the fog-trap was connected to the second condenser, while the remaining two were sealed. As this arm became charged with condensed tar (indicated by an increase of pressure on the gauge) a second arm was used, and the first one sealed. Similarly, as the second arm became charged the third one was used.

Examination of the Tar.

At the end of a distillation the electric current was switched off, and the apparatus allowed to cool in a current of coal gas. The fog-trap was now separated from the first condenser, and the remaining portion washed out with hot alcohol into a large-necked flask. This flask with its contents was now used as extraction flask for the fog-trap, the construction of which enabled it to be used as a self-Sohxlet (fig. 3).

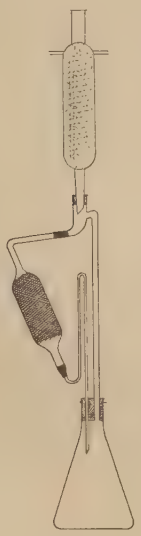


Fig. 3.

This particular fog-trap has been used during some thirty large-scale distillations of both coal and peat, and has been completely freed of tar each time by the Sohxlet method. It happens, on some occasions, that a small amount of dust from the retort is carried over into the glass wool, but this can be removed with chromic cleaning mixture.

The water was run off from the second condenser and measured in a graduated cylinder. As the remaining oil contained fractions with boiling points higher than 120°, it was transferred to a weighed flask and distilled up to 120°. Oil remaining from this distillation was washed with hot alcohol into the conical flask containing the tar from the first condenser. Evaporation of the alcohol left the total "heavy" tar as a solid mass in the conical flask. A conical flask was used, as the large surface area effective for the evaporation of the solvent minimised the danger of loss by sudden frothing of the tar and alcohol.

Repeated extractions with ether now removed the major portion of the tar, the ethereal extract being filtered through a weighed Sohxlet thimble into a weighed conical flask. Hot acetone was used to extract wax from the residue. Treatment of the final residue with boiling alcohol removed a resin, and left a small amount of dust, which had been carried from the retort during the dis-

tillation. The Sohxlet thimble, when weighed and dried, gave the weight of this dust; it was usually about one gram.

As the ether-soluble fraction contained the acids and bases, it was re-dissolved in ether, and extracted with 5 % sodium hydroxide. The alkaline extract was thoroughly washed with ether, and the washings re-extracted with 5 % sodium hydroxide, the ethereal residue from this extraction being added to the ethereal solution left after the first extraction with dilute sodium hydroxide. The latter alkaline extract was again washed with ether, and the washings returned to the other residues. Coal tar, when extracted in this manner, gives a dark-coloured, clear, alkaline solution of the tar acids; but, with an ethereal solution of peat tar, a bulky, gelatinous mass separated out. By removing this material and, after draining free from sodium hydroxide, washing with water and finally with acetone to remove adhering tar, it was obtained as a light brown, waxy substance. Further washing with water gave a pale creamy colour. The acetone washings were distilled to remove solvent, and the resulting tar redissolved in ether, and added to the original ethereal solution. This waxy solid was dried at 100°, and proved to be a mixture of sodium salts of solid acids from the peat tar. By Sohxletting with alcohol, it was divided into two fractions, the major portion being soluble in hot alcohol. The acids, on removal by heating with hydrochloric acid, and purifying from solution in benzene, were obtained as cream-coloured waxes. So far they have not been identified; the acids from both fractions are probably mixtures. The alkaline extract from low temperature coal tar also contains phenate-soluble materials of an amorphous nature; the amount of these substances present is considerable. Morgan (J.S.C.I., 1928, **47**, 551 T.) removed 19 % of the coal tar by treating the alkaline extract with saturated brine. In the case of peat tar, however, the amount of the material is negligible, being only 0·35 % of the total tar. They were separated as a gelatinous mass by treating the alkaline extract with petroleum.

Bases were next removed with 5 % sulphuric acid in a similar manner to the acids. A small amount of a black amorphous solid is also precipitated by the acid. Concentrated sulphuric acid removed the unsaturated compounds and left the neutral oil, consisting of wax and heavy oil. The wax was separated in a pure white state by freezing out from an alcoholic solution of the neutral oil, leaving heavy oil of a light brown colour.

Acidic constituents from the peat tar.

Dilute sodium hydroxide solution removes 30 % of the tar, and, in this respect, low-temperature peat tar is comparable with low-temperature coal tar, a distinctive feature of the latter being the high percentage of material that may be extracted with dilute alkali.

The alkaline extract of the tar was neutralised with dilute sulphuric acid and the tar acids liberated. The acids were not again completely soluble in

ether, an amorphous brown powder being thrown out. This amorphous powder was separated, and the ether evaporated from the acids. Petroleum ether now removed the true phenols, leaving a viscous mass. After extraction with ether this leaves an amorphous residue. Petroleum gives another amorphous precipitate from the ethereal extract. These three amorphous products are phenolic, and of a resinous character. Similar products were obtained from coal tar by Morgan, who adopts the name "resinols" for them, "as recalling their two outstanding characteristics." These "resinols," when dissolved in various organic solvents, give solutions which furnish lacquer-like surfaces on evaporation of the solvent.

Basic constituents of the peat tar.

The acid extract of the tar on standing precipitated a dark brown powder. On neutralising the extract with alkali, and extracting with ether, a second amorphous powder was obtained, the bases remaining in ethereal solution. Both these amorphous substances resemble Morgan's "resamines," giving glossy films when a solution in an organic solvent is evaporated.

The tar water.

Ammonia was estimated by rendering the tar water alkaline with sodium hydroxide solution and distilling, the distillate being received in standard acid.

The aqueous residue from the ammonia distillation was filtered, concentrated and re-filtered into a glass retort. By distilling to incipient dryness with syrupy phosphoric acid, adding water and re-distilling several times, the acetic acid was liberated. The distillate was received in standard sodium hydroxide solution, the excess sodium hydroxide being titrated with standard sulphuric acid, using phenol phthalein as indicator.

TABLE II.

Tar fractions calculated as percentages of the total tar.

	Black Peat.	Brown Peat.
Tar water, c.c. per 100 g. air dried ...	30	30
" " " " 100 g. anhydrous ...	22	21
Total tar (percentage anhydrous peat) ...	16·64	14·41
Tar fractions (percentage total tar) ...		
Light oil, B.P., up to 120°	8·50	9·03
"Heavy" tar	91·50	90·95
(*a*) Wax soluble in acetone	2·46	2·52
(*b*) Resin soluble in alcohol	1·26	1·88
(*c*) Tar soluble in ether	87·78	86·55
1. Alkali extraction	30·64	40·33
2. Dilute H_2SO_4 extraction ...	3·31	6·19
3. Unsaturated compounds ...	3·43	3·64
4. Neutral oil	50·40	36·39

Tar water as distilled from air-dried peat.

		Black Peat.	Brown Peat.
Ammonia	grams per litre	0·75	1·15
Acetic acid	of tar water	33·68	32·53

Calculating these yields as pounds per ton of air-dried peat, the following figures are obtained:—

	Black Peat.	Brown Peat.
Ammonium sulphate ...	17·4	30·2
Acetic acid	22·6	21·8

The ammonia and acetic acid contents of the tar water are also shown in the above table, which shows the main differences between the tars from the brown and the black peats. The former figures have been reduced to pounds of ammonium sulphate and acetic acid per ton of peat, as giving a better idea of their value from a commercial point of view.

It will be noticed that the tar from the brown peat, while being smaller in yield than that from the black, contains a higher percentage of materials which may be extracted with dilute alkali and dilute acid. The light oil fraction of the peat tar is also increased.

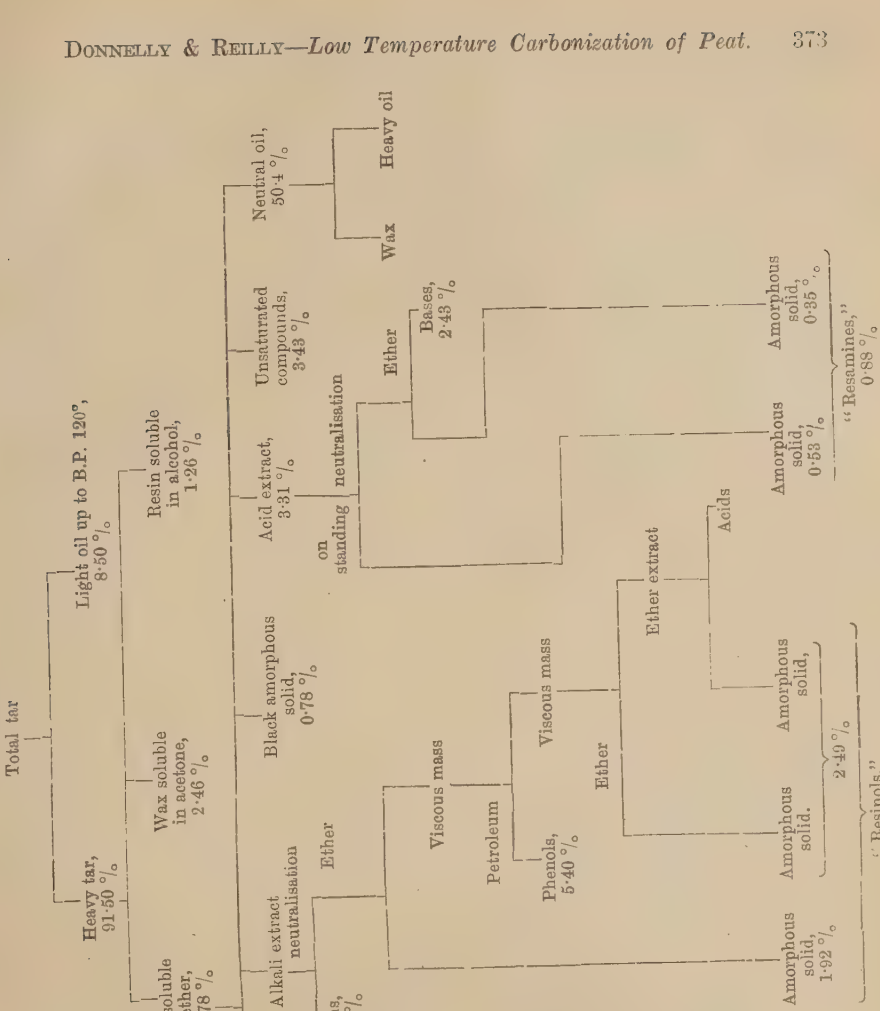
In Table III is shown the scheme for dividing the tar into fractions; the percentages given are for tar obtained from black peat. The striking feature of the results given in Table II is the high yield of tar obtained on low-temperature carbonization from both the black and the brown peats. Similar high tar results were obtained from a very fibrous mull peat from the Drimoleague district. This peat contained 28 % of water in the air-dried condition, and on low-temperature carbonization gave a tar yield of 20·5 % calculated on the anhydrous peat, the light oil fraction being 9·2 % of the total tar. Pyne and Reilly (Sc. Proc. R.D.S., **18**, No. 27) distilled this particular peat at 300° under a reduced pressure of 12 mm., and obtained 17·2 % of tar, calculated on the anhydrous peat.

Davis (The uses of peat, Department of the Interior, Bureau of Mines, Bulletin 16) refers to the quantity of tar that may be recovered from the distillation of peat in retorts. He remarks that the yield of tar rarely exceeds 4 or 4·5 % of the dry peat, so that the yields obtained in the present work are very exceptional, and point to the fact that low-temperature carbonization under the conditions described in this work apparently prevents the cracking of the heavier tar and oils to gaseous matter.

Non-condensible gases and other products from low-temperature peat distillation.

As the distillation of 500 g. of air-dried peat yielded a volume of approximately 31 litres of gas, it was necessary to conduct a distillation on a smaller scale to obtain a sample of the gas for analysis. Accordingly a weight of the air-dried peat equivalent to 10 g. of anhydrous peat was distilled. The distillation was carried out in a closed circuit in a current of nitrogen.

TABLE III.


Total tar
Heavy tar, 91·50 %
Light oil up to B.P. 120°, 8·50 %
Tar soluble in ether, 87·78 %
Wax soluble in acetone, 2·46 %
Resin soluble in alcohol, 1·26 %
Solid sodium salts of higher acids, 6·02 %
Alkali extract neutralisation
Ether
Ulmins, 0·36 %
Black amorphous solid, 0·78 %
Acid extract, 3·31 %
Unsaturated compounds, 3·43 %
Neutral oil, 50·4 %
Heavy oil
Wax
on standing
neutralisation
Ether
Bases, 2·43 %
Sodium salts insol. in alcohol, 1·38 %
Viscous mass
Petroleum
Phenols, 5·40 %
Viscous mass
Ether
Ether extract
Acids
Amorphous solid, 0·53 %
Amorphous solid, 0·35 %
"Resamines," 0·88 %
Sodium salts soluble in alcohol, 4·64 %
Higher acids, 4·24 %
Higher acids, 1·11 %
Amorphous solid, 1·92 %
Amorphous solid.
Amorphous solid,
2·49 %
"Resinols," 4·41 %

The circuit, which was similar to the one used for distillations of small samples of coal in previous work, is shown in fig. 4. The peat was placed in a glass retort, 16 × 2·8 cms., the retort being encased by a small electric furnace capable of reaching a temperature of 550° in 3 hours, or less if desired. A first condenser of the same type as that used during the large-scale distillation was kept at a temperature of 120°, and condensed tar with a boiling point over 120°. One tube of glass wool was sufficient to trap the "tar fog." Water and light oil were condensed as before in a second condenser at −20°, a tube of tightly packed glass wool ensuring that no trace of fog remained uncondensed. As with coal, a type of compound is evolved during peat distillations that can be absorbed by phosphorus pentoxide, and this was removed after the vapours had passed through the cotton wool; the phosphorus pentoxide became first yellow and then black. Light spirit was removed by a U tube of activated carbon, which had been dried to constant weight in a current of dry air at 105°.

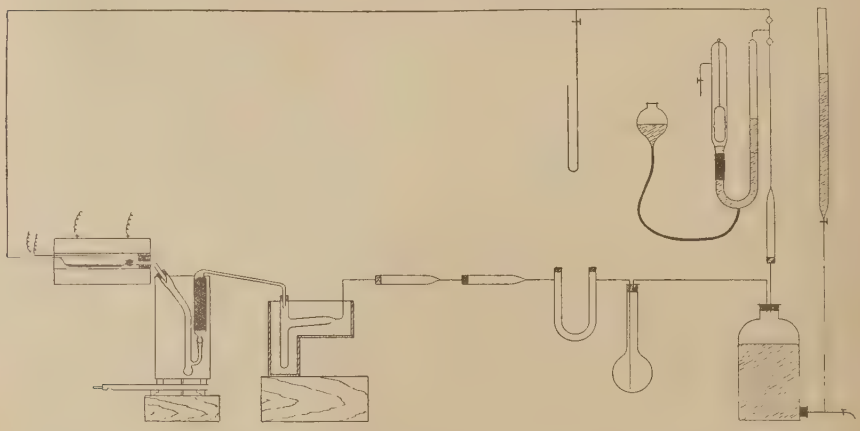


Fig. 4.

The scrubbed gas, after leaving the activated carbon, passed through a mixing flask, and finally to a gas reservoir. This consisted of a two-litre bottle fitted with a tap at the bottom and a three-holed rubber bung at the top. A burette connected to the lower tap enabled mercury to be run into the reservoir, while a special tap leading from the top was used for sampling the gas. After leaving the reservoir, the scrubbed gases passed through a guard tube of phosphorus pentoxide and asbestos fibre (this was a precaution against moisture from the mercury being carried into the circuit), and were pumped by means of the special mercury oscillating pump over the peat in the retort. A liquid paraffin gauge between the pump and the retort indicated the pressure in the circuit, which was kept at atmospheric by adjustment of the mercury in the reservoir.

Before commencing a distillation the absorption tubes and condensers were weighed, and all joints sealed with paraffin wax. The volume of the apparatus

was now obtained as described by us in previous work on coals (J.S.C.I., 1928, **47**, 189 T.), and the apparatus filled with nitrogen (J.S.C.I., 1928, **47**, 189 T.). When a temperature of 550° was reached in the retort, further heating was continued for ten minutes, and the electric current switched off. The first condenser bath and the freezing mixture for the second condenser were removed, and the apparatus allowed to cool to room temperature. During cooling, mercury was run into the reservoir, so that the gauge remained at constant level. The difference between the volume of mercury run out of the reservoir, during the distillation, and the volume run in, during cooling, gave the volume of gases evolved. Samples of gas for analysis were drawn off through the gas-sampling tap of the reservoir, and the gas-mixing flask was disconnected and weighed, the exit and entrance tubes being closed with screw clips. Dry air was now drawn through the flask and remaining parts of the circuit for ten minutes and the weighings carried out. The use of the mixing flask in the circuit enabled the density of the mixed gases to be obtained, thus serving as a check on the weight of gas evolved, which was found by difference.

In Table IV are given the results from a black peat distillation calculated as percentage weights of the anhydrous peat.

TABLE IV.

Peat charcoal	46·17
Tar plus water	38·2
Light spirit (absorbed by activated carbon) ...	3·15
Phosphorus pentoxide absorption	3·87
Gas	8·61

The results for the yields of coke and of tar plus water for the large-scale experiments agree with the above remarkably well, these yields being 46·1 % and 38·0 % respectively.

Analysis of the gases.

The gas on analysis gave the following composition :—

Carbon Dioxide (CO_2)	41·87 %
Carbon Monoxide (CO)	34·20 %
Hydrogen (H_2)	2·38 %
Unsaturated Hydrocarbons and Ethane (C_2H_6) ...	13·23 %
Methane (CH_4)	8·32 %

Ryan (Reports upon the Irish peat industries, Pt. ii : Econ. Proc. R. Dub. Soc., **1**, pp. 520–521) gives the following as indicating the composition of peat gas :—

Carbon Dioxide (CO_2)	30 %
Carbon Monoxide (CO)	14 %
Hydrogen (H_2)	19 %
Methane (CH_4)	30 %
Heavy hydrocarbons	7 %
Nitrogen	Trace.

Free wax and bitumen in peat.

Peat in the raw condition contains free wax and bitumen in varying quantities. Samples of the peats used in this work were extracted with acetone, and gave high yields of this wax. The black peat contained 10·47 % of wax, a very high value, while the brown peat gave 8·24 %.

Summary.

The work just carried out is a preliminary examination of a peat from one particular district of Co. Cork. From the yields of tar obtained on low-temperature carbonization of this peat it is evident that this means of distillation prevents cracking of the heavy tar to a very great extent, preserving, at the same time, the wax and heavy oil.

A yield of 16·64 % of tar, calculated on the anhydrous peat, was obtained from air-dried black peat.

The phenols content of the tar was 5·40 %. Higher acids of the nature of waxes (at present unidentified) have been obtained from peat tar acids.

"Resinols" and "resamines," two types of compounds which have been found in the alkali and acid extractions from low-temperature coal tar, have also been isolated from low-temperature peat tar. The "resinols" amount to 4·41 % of the tar and the "resamines" to 0·88 %.

A yield of 22·6 pounds of acetic acid per ton of air-dried peat was obtained. Davis (The uses of peat, Dept. of the Interior, Bureau of Mines, Bulletin 16) gives 12·6 pounds of acetic acid per ton of air-dried peat as being a good yield.

The same writer gives 9 pounds of Ammonium Sulphate per ton of air-dried peat as being a fair yield. The authors obtained 17·4 pounds by the low-temperature method.

The percentage weight of the gas evolved is low, being only 8·61 % of the anhydrous peat. The gas is of a poor quality, containing 41·87 % by volume of carbon dioxide, while the combined hydrogen and hydrocarbon content is only 23·91 %.

The particular peat under observation contains 10·47 % of wax and bitumen. An investigation is at present in progress as to how the presence of this wax affects the tar obtained during low-temperature carbonization of the peat.

The authors desire to thank the Royal Dublin Society for the provision of the calorimeter used in the above work.

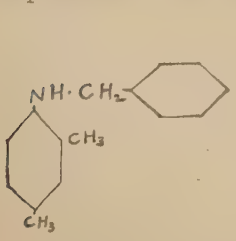
No. 30.

THE NITRATION OF SUBSTITUTED PHENYLBENZYLAMINE DERIVATIVES.

By J. REILLY, T. V. CREEDON, and P. J. DRUMM.

[Read November 26, 1929. Published separately February 8, 1930.]

In a recent study of benzylaniline (J. C. S. Trans., 1928, 563) and of some phenylbenzylamine derivatives (J.C.S. Trans., 1929, 641) the authors have shown that the nitration of such substances as free bases leads to the formation of nitro derivatives substituted in the aniline ring, whilst their nitration as salts promotes substitution in the benzyl nucleus. It was further shown that whilst benzylaniline does not nitrate in acetic acid solution (forming only the nitrate of the base), the replacement of the imino hydrogen atom by the nitroso group facilitates nitration to a remarkable degree. This work has now been extended to a study of phenylbenzylamine derivatives containing substituents in the aniline ring, and in the first instance benzyl-m-4-xylidine was chosen as representative of such a type.



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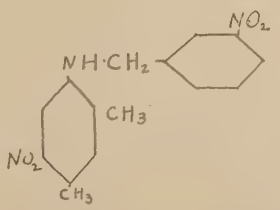
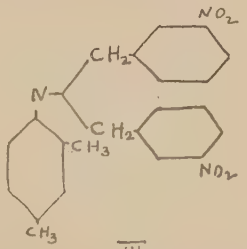


II



III

Benzyl-m-4-xylidine (1) was first prepared by Jablin-Gonnet (Bull. Soc. Chim., 1891 (3), 6, 21) by the prolonged heating of m-4-xylidine and benzyl chloride. On nitration of this substance an orange-coloured nitro derivative was isolated, for which neither the melting point nor the orientation of the nitro groups in the molecule was established. The authors have now prepared this substance by a more convenient method, and have found that on nitration of benzyl-m-4-xylidine, a nitro group enters each ring with the formation of 6-nitro-1 : 3-dimethylphenyl-3-nitrobenzylamine. The constitution 6-nitro-1 : 3-dimethylphenyl-3-nitrobenzylamine (II) follows from the synthesis of the latter compound from 6-nitro-m-4-xylidine and m-nitrobenzyl chloride.

In determining the constitution of this substance, the following new nitrobenzyl and benzylnitroxylidines have been synthesized, viz., 2, 3, and 4-nitro-

benzyl-m-4-xylidines, 6 nitro-1 : 3-dimethylphenylbenzylamine, and 1 : 3-dimethylphenyldi-m-nitrodibenzylamine.

Experimental.

Preparation of Benzyl-m-4-xylidine.

Benzyl chloride (1 mol.) and m-4-xylidine (2 mols.) (purified by Limpach's method (G.P. 39, 947)) were mixed in the cold, no heat being developed. The mixture was gently warmed on the water bath when, at 90°, a vigorous reaction set in, the temperature rising to about 110°. A colourless, crystalline solid, which proved to be m-4-xylidine hydrochloride, separated. The whole was allowed to stand, out of contact with air, for twelve hours, and was finally heated on a water bath to complete the reaction. The hydrochloride was filtered off and washed with anhydrous ether. The filtrate, after removal of ether, was distilled in steam to remove unchanged benzyl chloride, and the residue taken up with ether and dried over anhydrous potassium carbonate. On removal of the ether the remaining oil was distilled under diminished pressure, when benzyl-m-4-xylidine passed over at 236°/17 mm. (Jablin-Gonnet gives b.p. 200–210°/15 mm.) as a colourless oil, which darkened in colour on prolonged standing. (Found : N, 6·6 %, $C_{15}H_{17}N$ requires N, 6·6 %.)

Nitration of Benzyl-m-4-xylidine.

To a solution of benzyl-m-4-xylidine (5 g.) in concentrated sulphuric acid (75 c.c.) was slowly added, with stirring, a mixture of nitric acid (d. 1·51; 3 g. 2 mols.) and concentrated sulphuric acid (10 c.c.), care being taken to maintain the temperature below 0°. The mixture was stirred for three hours at 0° and poured on crushed ice. A yellow solid separated, which was collected, washed with water and dried. From the solution of this solid in alcohol there separated, on cooling, a yellow solid (yield 4·5 g.), which on further crystallisation from alcohol was obtained as bright yellow prisms, m.p. 152–153°. (Found : N, 13·8 %, $C_{15}H_{15}O_4N_3$ requires N, 13·95 %.) This substance was identified as 6-nitro-1 : 3-dimethylphenyl-3-nitrobenzylamine by the synthesis described below. The alcoholic mother-liquor from the original solution was concentrated and yielded an oily solid from which on fractional crystallization a further small quantity of the above dinitro body was isolated.

When benzylxylidine was nitrated in sulphuric acid under exactly similar conditions, using only 1 mol. of nitric acid, the same nitro body was isolated, but in smaller yield, a considerable amount of benzyl-m-4-xylidine being recovered unchanged.

Synthesis of 6-nitro-1 : 3-dimethylphenyl-3-nitrobenzylamine (II).

6-nitro-m-4-xylidine (1 mol.) and m-nitrobenzyl chloride (1 mol.) were heated, under reflux, in a 20 per cent. solution of sodium hydroxide for five to six hours. The product, which solidified on cooling, was filtered, washed with water and extracted with boiling alcohol.

There separated, on cooling, yellow prisms, which melted, alone or when mixed with the above nitro body at 152–153°. (Found: N, 13·85 %, $C_{13}H_{15}O_4N_3$ requires N, 13·95 %.) 6-nitro-1 : 3-dimethylphenyl-3-nitrobenzylamine is readily soluble in warm chloroform, acetic acid, benzene, and ethyl acetate, and sparingly soluble in cold ether and cold alcohol.

Synthesis of nitrobenzylxylidines.

2-*nitrobenzyl-m*-4-*xylidine*.—M-4-xylidine (2 mols.) and o-nitrobenzyl chloride (1 mol.) were heated in absolute alcoholic solution under reflux for five hours.

On cooling, a yellow solid separated, which on further crystallization from alcohol was obtained as orange-coloured needles, m.p. 83°. (Found: N, 10·8 %, $C_{15}H_{16}O_2N_2$ requires N, 10·94%.) 2-nitrobenzyl-m-4-xylidine is readily soluble in the cold in chloroform, benzene, ethyl acetate, and ether.

3-*nitrobenzyl-m*-4-*xylidine* was prepared similarly. It separated from alcohol as an oil which slowly solidified on keeping in the ice chest. It was obtained from petroleum ether (B.P. 40–60°) as bright yellow prisms, m.p. 70°. (Found: N, 10·9 %, $C_{15}H_{16}O_2N_2$ requires N, 10·94 %.) 3-nitrobenzyl-m-4-xylidine is soluble in the cold in chloroform, benzene, ether, and ethyl acetate.

4-*nitrobenzyl-m*-4-*xylidine* was obtained from alcohol in orange-coloured prisms, m. p. 93°. (Found: N, 10·8 %, $C_{15}H_{16}O_2N_2$ requires N, 10·94 %.) 4-nitrobenzyl-m-4-xylidine is readily soluble in the cold in chloroform, benzene, ether, and ethyl acetate.

Synthesis of 6-*nitro*-1 : 3-*dimethylphenylbenzylamine.*

Benzyl chloride (1 mol.) and 6-nitro-m-4-xylidine (1 mol.) were heated under reflux in concentrated sodium hydroxide solution for ten hours.

The solid which separated on cooling was extracted with warm dilute sulphuric acid to remove any unchanged nitroxylidine. The insoluble portion was washed with warm water and taken up with alcohol, from which it separated as yellow elongated prisms, m. p. 135°. (Found: N, 10·8 %, $C_{15}H_{16}O_2N_2$ requires N, 10·94%.) 6-nitro-1 : 3-dimethylphenylbenzylamine is readily soluble in cold chloroform, but sparingly so in cold ethyl acetate, ether, and benzene.

Synthesis of 1 : 3-*dimethylphenyl-di-m-nitrodibenzylamine* (*III*).

M-4-xylidine (1 mol.) and m-nitrobenzyl chloride (2 mols.) were heated in alcoholic solution for six hours. The alcohol was removed, a concentrated aqueous solution of sodium carbonate added and the mixture boiled under reflux for nine hours. A warm alcoholic solution of the product yielded on cooling pale yellow needles, m.p. 116°. (Found: N, 10·9 %, $C_{22}H_{21}O_4N_3$ requires N, 10·7 %.)

The authors desire to thank Miss M. Kingston for assistance in the earlier part of the work.

Chemical Department,
University College, Cork.

No. 31.

A STUDY OF TWO NEW SPECIES OF BACTERIA BELONGING TO THE GENUS *CHROMOBACTERIUM*.

By M. GRIMES, M.Sc., Ph.D.,
Department of Dairy Bacteriology, University College, Cork.

[Read November 26, 1929. Published separately February 8, 1930.]

In the course of the bacteriological examination of thirty-six samples of water, bacteria belonging to the genus *Chromobacterium* were isolated in seventeen cases. These seventeen samples of water were taken, either from surface wells, or from deep wells that the bacteriological examination showed to be contaminated by the admixture of surface waters. The waters were plated in duplicate in dilutions of 1 c.c., 1/10 c.c., and 1/100 c.c., using lactose nutrient agar, and the Petri dishes incubated at 37° C. for two days, and at 21° C. for seven days.

The number of colonies of bacteria belonging to the genus *Chromobacterium* that were found on the Petri dishes incubated at 21° C. for a week was generally less than 10 per c.c., and usually accompanied by bacteria belonging to the genus *Pseudomonas*. Bacteria belonging to the genus *Chromobacterium* were never found on the corresponding Petri dishes incubated at 37° C.

Sixteen of the seventeen cultures examined resembled one another so closely that they were considered to be the same species and are represented by V 1. The sixteen cultures closely resembled one another morphologically, but differed slightly in the rate of development of the violet pigment, in the rate of liquefaction of gelatine, and in the type of digestion of sterile milk, but these differences were not considered marked enough for them to be regarded as different species. This type occurs in many parts of Ireland, having been isolated from samples of water received for bacteriological examination from County Cork, County Limerick, County Tipperary, and County Galway, and it has been named *Chromobacterium hibernicum*.

The culture known as V 3 was isolated from a sample of water drawn from a newly bored artesian well, sunk to a depth of 66 feet. The total bacterial count at 21° C. was 5,200 per c.c., and only the one colony was found. The growth form of this bacterium is characterized by its dark violet sheen and its tenacity. It tends to come away from the medium on which it is grown as a film, and the growth can be lifted off the medium in large patches by inserting

a platinum needle under it. In consequence, it has been named *Chromobacterium cohaerens.*

Both species of bacteria reduce nitrates, whereas all the species listed in Bergey's "Manual of Determinative Bacteriology" are stated not to reduce nitrates. *Chromobacterium cohaerens* has a positive diastatic action, whereas *Chromobacterium hibernicum* is negative.

V 1.

Found in water from surface wells.

Morphology.

Slender rods 1·0μ to 1·75μ by 0·5μ to 0·75μ, aerobic, motile, non-spore-forming, gram-negative, may be gram-variable.

Cultural Characters at 21° *C.*

Nutrient Agar.—Seven days—surface colonies—may be circular 1 to 6 mm. diameter, or irregularly shaped 3 to 8 mm. by 2 to 4 mm.—grayish at first, violet pigment starts to develop in from 2 to 4 days at edge of colonies and spreads inwards towards centre. Colonies glistening, raised, opaque, finely granular; edge definite, entire. Sub-surface colonies 1 to 2 mm., oval, do not develop pigment for several days.

Nutrient Agar slant. — Seven days—growth good, grayish at first, turning violet at the edges, violet pigment spreading inwards towards the centre. Growth glistening, smooth, raised, opaque; definite edge, entire or undulate.

Nutrient agar stab.—Seven days—good growth, violet pigment on surface. Growth grayish along line of stab.

Nutrient gelatine.—Five days—slight to fair liquefaction, colonies circular, granular, grayish colour at first, turning violet, edge entire.

Nutrient gelatine stab.—Ten days—gelatine one-sixth liquefied, stratiform. filiform growth along line of stab, violet pigmented growth in the liquefied gelatine. Gelatine two-thirds liquefied in from three to six weeks.

Potato slope.—Seven days—good growth, colour at first brownish, finally dark violet, glistening, raised, rugose, opaque, definite edge.

Physiological Characters at 21° *C.*

Nutrient broth.—Seven days—growth, cloudiness, violet pigmented film on surface, and violet coloured sediment; pigment diffused through liquid.

Dunham's solution.—Seven days—growth, cloudiness, violet pigmented film on surface, violet pigmented deposit at bottom of test-tube.

Fermentation.—Ten days—neither acid nor gas formed in galactose, glycerol, glucose, inulin, lactose, levulose, maltose, mannitol, salicin, and saccharose broths. Development of violet pigment on surface of sugar broths.

Plain milk. — Two to four days—growth, violet pigment on surface, violet colour diffused through upper layer of milk. Ten days—upper part of milk of a dense dark violet colour, with dark violet film on surface. Violet colour diffused through milk and dark violet sediment. Soft coagulation and partial digestion of milk in from four to six weeks. Slight increase in acidity from 0·17 to 0·20 per cent. lactic acid. Total count (five days) = 400,000,000 per c.c.

Litmus milk. — A slight development of acidity, with the same changes taking place as described under "Plain milk."

Potato utilization as indicated by hydrogen peroxide (H_2O_2) (Gull, Jean, and Broadhurst). H_2O_2 positive.

Diastatic action—negative.

Indol—negative.

Nitrates—reduced.

Remarks—growth scanty or absent at 37° C.

The name suggested for this bacterium is *Chromobacterium hibernicum.*

V 3.

Found in water obtained from a recently sunk artesian well, 66 feet deep.

Morphology.

Rods 1·25μ to 3·0μ by 0·75μ to 1·0μ, aerobic, non-spore-forming, motile, generally gram-negative, may be gram-variable, may form chains (especially noticeable when grown in gelatine media).

Cultural Characters at 21° *C.*

Nutrient agar. — Four days—colonies 2 to 5 mm. diameter, dark violet, glistening, raised, butyrous, opaque, finely granular, generally circular, edge entire or slightly indefinite. Sub-surface colonies, oval 1 to 2 mm. long, do not develop pigment for several days.

Nutrient agar slant. — Seven days—growth good, dark violet, glistening, smooth to rugose, opaque, raised, edge entire. The growth is characterized by its tenacity, the growth can be lifted off media in large patches by inserting needle under it.

Nutrient agar stab.—Seven days—good grayish growth along line of stab, grayish to dark violet pigment on surface.

Nutrient gelatine.—Five days—marked liquefaction—colonies sunk—diameter 1 to 3 mm., granular, opaque, grayish at first, finally violet, edge entire or slightly irregular.

Nutrient gelatine stab.—Ten days—gelatine one-quarter to one-half liquefied, saccate, filiform grayish growth along line of stab. Growth in liquid grayish to violet. The development of violet pigment is not as marked as in *Chromobacterium hibernicum.*

Potato slope.—Seven days—growth poor to fair, glistening, raised, opaque, rugose, dark violet, definite edge.

Physiological Characters at 21° C.

Nutrient broth.—Seven days—growth, cloudiness, grayish film on surface turning violet, grayish violet sediment.

Dunham's solution.—Seven days—growth, cloudiness, gradual development of violet pigment on surface and violet pigmented deposit at bottom of test-tube.

Fermentation.—Ten days—neither acid nor gas formed in galactose, glycerol, glucose, inulin, lactose, levulose, maltose, mannitol, salicin, and saccharose broths.

Plain milk.—No evident change for from twenty-four to forty-eight hours, then slight grayish to bluish violet pigment develops at surface, and in ten days coagulation with soft curd, and development of violet pigment at surface of milk. Partial digestion of milk in from two to four weeks. Total count (five days) = 300,000,000 per c.c.

Litmus milk.—No marked development of either acidity or alkalinity, the same changes taking place as described under "Plain milk."

Potato utilization as indicated by hydrogen peroxide (H_2O_2) (Gull, Jean, and Broadhurst). H_2O_2 positive.

Diastatic action—positive.

Indol—negative.

Nitrates—reduced.

Remarks—Growth scanty or none at 37° C.

The name suggested for this bacterium is *Chromobacterium cohaerens.*

Grateful acknowledgment is made of the kindness of Dr. R. St. John-Brooks, Curator, National Collection of Type Cultures, Lister Institute of Preventive Medicine, London, in confirming the reduction of nitrates by *Chromobacterium hibernicum* and *Chromobacterium cohaerens*, and in forwarding type cultures for comparison. Acknowledgment is also made of the kindness of Dr. G. H. Weaver, Curator, American Type Culture Collection, Chicago, U.S.A., in forwarding a type culture for comparison.

No. 32.

THE THERMAL INSTABILITY OF THE EARTH'S CRUST.—II.

By J. H. J. POOLE, Sc.D.

[Read November 26, 1929. Published separately March 12, 1930.]

In a previous paper under the same title, published in the Philosophical Magazine for March, 1928, it was shown by Dr. H. H. Poole and myself that the possible stability of the earth's crust appears to depend on whether the increase of melting point temperature of basalt with depth is greater or less than the increase of temperature with depth in a column of liquid basalt in adiabatic equilibrium. If, as the available data seemed to indicate, the melting point gradient was the greater, then it follows that a basaltic crust containing more than a certain definite proportion of radio-active material will not attain a steady thermal state, but will go through a series of partial liquefactions and resolidifications, with corresponding cyclic changes in the temperature gradient of the surface materials.

Since the publication of that paper it has, however, occurred to me that possibly the mathematical side of the problem might be a little further advanced by some fresh considerations. To deal with nearly any highly complicated physical problem mathematically, we are, of course, nearly always compelled to make rather sweeping simplifying assumptions, and it is in our choice of these assumptions that we are most liable to be misled. In the actual problem of the earth's crust affairs are so complicated by the inhomogeneity of the crust, the probable decrease of radio-activity with depth, the fact that the materials involved have not a very definite melting point, and many other considerations too numerous to mention, that it would seem impossible to deal directly with the question. It is accordingly proposed to consider the much simpler case of a homogeneous crystalline crust of definite melting point and constant radio-activity. Furthermore, all complications due to the presence of overlying materials of higher melting point or to tidal effects and possible lateral convection currents in any liquid portions of the crust will be neglected.

The problem then really reduces to the following:—

Given a long vertical column of a crystalline solid containing a definite proportion of radio-active matter, the whole column being enclosed in a non-conducting cylinder with a closed bottom and open top, so that heat can only enter or leave the system at the upper surface, and given the state of the system at any time, determine its past and future history.

It is obviously justifiable to make the sides of the cylinder non-conducting,

since the temperature at a fixed depth in the earth's crust is being taken as the same everywhere, the effect of the inhomogeneity of the crust being neglected. Thus there will be no lateral flow of heat, and this is equivalent to a non-conducting cylinder wall. By assuming the bottom of the cylinder to be also non-conducting, we are neglecting any possible escape of heat from the sub-crustal materials. This is perhaps not the case in actuality, but, if it can be shown that periodic variations of state occur in the system postulated, then it would seem that a small steady inflow of heat at the bottom of the column would not alter the result seriously. The temperature of the upper surface of the column will be taken as constant, since the surface temperature of the earth's crust over long periods is practically fixed, depending, as it does, nearly entirely on solar radiation, and not on the small heat flow from the earth itself. Furthermore, it is to be assumed that the melting point pressure curve for the crystalline solid is steeper than the adiabatic temperature pressure curve for the liquid state. As already stated in the previous paper (*loc. cit.*), this condition appears to be fulfilled for basaltic materials.

It may easily be shown that in such a column, provided its length does not exceed a certain definite value depending on the percentage of radio-active matter, an equilibrium state will finally be attained, when θ the temperature at the depth h, is given by

$$\theta = \theta_0 + ah - qh^2/2K$$

where

θ_0 = surface temperature,

a = temperature gradient near surface,

q = number of calories generated per second per c.c. by the radio-active materials,

K = thermal conductivity.

We assume K to be independent of θ and h.

If, however, the column is sufficiently long, the temperature θ given by the above equation will be greater than the melting point temperature at the same point for the lower layers of the column. The consequence is that, as soon as the temperature at any point reaches the melting point, no further rise of temperature takes place, but melting of the solid commences. The subsequent course of events will depend on the initial conditions, but it will perhaps first be desirable to consider the general case of the instability of a melted layer in such a column.

Let the state of affairs at any time be as represented in fig. 1. The origin is taken at the base of the column, and x and y are the distances of the upper and lower surfaces of the liquid layer from this point. The lower solid portion is all just at its melting point, but the radio-active heat generated in it will be used up in slowly remelting it; and since this remelting will be very slow, and takes place probably in a honeycomb structure, we will assume that it is not

transferred to the main liquid layer. The temperature of the lower surface of the upper solid portion will be that of the melting point under the pressure at that depth. Call this temperature θ_1, and let α be rate of increase of melting point temperature with depth. Then the temperature of the upper surface of the lower basalt will be $\theta_1 + \alpha(x - y)$. For basalt α is probably about 3×10^{-5} °C. per cm. Hence the temperature of the bottom of the liquid layer must be at least $\theta_1 + \alpha (x - y)$. But the maximum temperature gradient possible in a liquid column in convective equilibrium is the adiabatic gradient. If the gradient exceeds this by even a small amount, convection currents are set up which soon bring the gradient down to the adiabatic. Let β be rate of increase of temperature with depth in a liquid column in adiabatic equilibrium. This quantity is about $0{\cdot}75 \times 10^{-5}$ ° C. per cm. for basalt. Thus, since the temperature of the base of the liquid layer is at least $\theta_1 + \alpha (x - y)$, the temperature of the top of the layer will be $\theta_1 + (\alpha - \beta) (x - y)$, i.e., the liquid in contact with the upper solid is hotter than it by an amount $(\alpha - \beta) (x - y)$. The consequence is that heat will flow from the liquid into the upper solid, and if this inflow of heat is greater than the outflow, due to conduction in the solid, some of the solid will melt, and the liquid layer gradually move upwards.

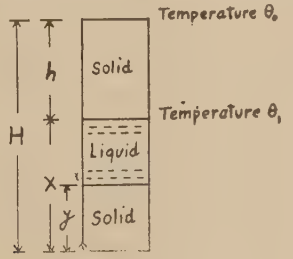


Fig. 1.

The first point to consider is the rate at which heat will flow from the liquid to the overlying solid. It is generally accepted that the heat loss from a hot surface immersed in a fluid is approximately proportional to $T^{\frac{5}{4}}$, where T is the temperature difference between the surface and the ambient fluid (Dictionary of Physics, vol. i, p. 477). Péclet concludes that for any body of linear dimensions over about 40 cm. the heat loss per cm.^{2} in air at ordinary pressure is approximately constant, and equals about $4 \times 10^{-5} T^{\frac{5}{4}}$ cals. per cm.^{2} per second. As this figure refers to air, it is not directly applicable. If, however, we assume that the cooling power of a fluid for similar bodies is constant, some results of A. H. Davis (Phil. Mag., November, 1922, p. 933) will enable us to form some idea of the corresponding figure for a liquid. Using the same heated wire, he found that the heat loss in calories per cm. length per second per degree excess of temperature varied from $0{\cdot}82 \times 10^{-4}$ for gases to about 7×10^{-4} for various liquids. Thus, if we assume that the cooling power of a

liquid is about nine times that of air, we will probably not be wrong by more than a factor of two or three. This would lead to the heat flow from a liquid to a solid surface being approximately $4 \times 10^{-4}\ T^{\frac{5}{4}}$ cals. per cm.^{2} per second. Furthermore, since, in our problem, T will always be small, it will be sufficiently accurate to write T for $T^{\frac{5}{4}}$. Thus the heat flow from the liquid to the solid $= kT$,

where $k = 4 \times 10^{-4}$ cals. per cm.^{2} per sec.

But since $T = (\alpha - \beta)(x - y)$,

the heat flow $= k(\alpha - \beta)(x - y)$

$= b(x - y)$,

where $b = k(\alpha - \beta)$ $= 8 \times 10^{-9}$ cals. per cm.^{2} per sec.

It will be shown later that the value we obtain for b from the above values of k, α, and β is too large, as it would make the system altogether too unstable. Probably the reason for this is that the liquid basalt will not act as a true fluid owing to its high viscosity, and that this reduces the value of b.

Another factor, which enters into the equations of motion of the liquid layer, is the temperature gradient in the solid immediately above the liquid layer. To express this in terms of known quantities would be extremely difficult, if not impossible. It is plain, however, that it must be a function of the depth of the upper solid and the time only, if the initial conditions are fixed. Let us accordingly denote it by $f(h, t)$, where h = depth of upper solid, i.e. $h = H - x$. As h decreases, it would seem correct to assume that $f(h, t)$ increases. It is to be remembered that h is also a function of t, the time. The rate of escape of heat from the lower surface of the upper solid crust by conduction will accordingly be $Kf(h, t)$ cals. per cm.^{2} per second.

We will take the cross-section of column to be 1 cm.^{2}

The inflow of heat from the liquid into the lower surface of the upper solid in a time $dt = b(x - y) \cdot dt$, while the outflow of heat due to conduction $= Kf(h, t) \cdot dt$.

The net gain $= [b(x - y) - Kf(h, t)]dt$.

This must be used in melting some of the bottom of the upper solid, and hence increasing x by an amount dx.

Let L = latent heat of fusion,

ρ = density.

Then we have $L\rho \cdot dx = [b(x - y) - Kf(h, t)]\, dt$

or $$L\rho \cdot \frac{dx}{dt} = b(x - y) - Kf(h, t).$$

The generation of heat in the liquid layer due to radio-activity $= q(x - y) \cdot dt$. The loss of heat of the layer at the upper surface is, however,

$b(x - y) . dt$. Thus the net loss $= (b - q)(x - y) . dt$. If, as is the case, $b - q$ is positive, then the only way for the layer to supply this loss is for some of the liquid, which becomes cooled by contact with the upper solid, to sink through the liquid, and partially resolidify under the increased pressure. This will occur, since the melting point gradient is steeper than the adiabatic temperature gradient actually existing in the layer. The resolidified portion, being denser, collects at the bottom of the column, and will increase y by an amount dy, given by the equation

$$L\rho . dy = (b - q)(x - y) . dt$$

or

$$L\rho . \frac{dy}{dt} = (b - q)(x - y).$$

If $b - q$ is negative, it is easy to see that a steady state will be attained. dy/dt will be negative, and therefore melting will occur both at the upper and lower surfaces of the liquid. The lower melting will continue till the bottom of the column is reached, and the whole liquid column will then rise above its melting point, since $qx > bx$, and the crust will become thinner until the loss of heat by conduction through the crust is exactly equal to the radio-active generation of heat in the liquid layer. This is a stable state, and no further change will occur.

In practice, however, $b - q$ is undoubtedly positive, which means that dy/dt is always positive, i.e., the bottom of the liquid will always move upwards as time advances. The top of the layer will also move upwards as long as

$$b(x - y) > Kf(h, t).$$

When $b(x - y) = Kf(h, t)$, the upper solid has its minimum thickness. Owing, however, to the fact that y is still increasing, $x - y$ will further diminish, and hence $b(x - y)$ will now become less than $Kf(h, t)$.

Solidification will then start to occur at the top of the liquid layer as well as at the bottom, and this will persist till the whole liquid layer finally disappears.

The maximum thickness of the liquid layer will occur when

$$dx/dt = dy/dt,$$

i.e.

$$b(x - y) - Kf(h, t) = (b - q)(x - y)$$

or

$$q(x - y) = Kf(h, t).$$

In fact, the upper solid has its minimum thickness when the loss of heat by conduction through it equals the loss of heat of the liquid layer by convection, and the liquid layer has its maximum thickness when the loss of heat by conduction is equal to the radio-active generation of heat in the liquid.

We are now in a position to consider the general course of events in the system. Our main difficulty is in the choice of the initial conditions. I propose to take the simplest case first, and assume that fig. 2 represents the initial state of the system.

The whole column is to be taken as completely solid except for a very thin layer CD at the base. The solid above B is in thermal equilibrium with its own heat supply, and the temperature at B is equal to the melting point. The solid below B is everywhere at its melting point, but completely solid. Owing to the fact that the melting point rises with depth, there will be slow loss of heat due to heat conduction. This loss is, however, very small, and would probably in the actual case be balanced by an inflow from the lower regions of the earth. We will accordingly assume that the part of the system BD is initially thermally isolated. The consequence is that, as time advances,

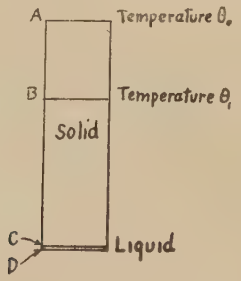


Fig. 2.

melting must gradually occur. This melting will take place probably in small cells, scattered through the whole mass of the column. These cells will, it is true, tend to move slowly up through the column, but as long as they are small their motion will be excessively slow. To enable us to deal with the question, it is assumed that initially a very thin layer of liquid is present at the bottom. This layer will gradually move upwards and sweep up all the liquid into itself as it does so. When it has reached B, the first stage of the thermal cycle is completed. In the first stage the question of escape of heat by conduction does not enter into the equations, and accordingly we can completely express them.

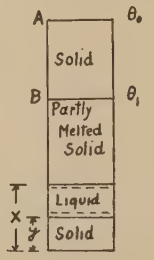


Fig. 3.

Let fig. 3 represent the condition of affairs at any time t.

When $t = 0$ we take $x = x_0$ and $y = 0$.

Suppose x increases by an amount dx in a time dt. The heat required to

melt a layer dx thick $= L\rho \,.\, dx$. This must be supplied partly by the radioactive heat accumulated in the layer since zero time, and partly by the transference of heat from the liquid in the time dt, i.e., we have

$$L\rho \,.\, dx = qt \,.\, dx + b\,(x - y) \,.\, dt$$

or

$$\left(L\rho - qt\right)\frac{dx}{dt} = b\,(x - y). \tag{1}$$

The consideration of the loss of heat by the liquid layer gives, as before,

$$L\rho \,.\, dy/dt = (b - q)\,(x - y).$$

Differentiating equation 1 with regard to the time, we have

$$\left(L\rho - qt\right)\frac{d^2x}{dt^2} - q \,.\, \frac{dx}{dt} = b\left(\frac{dx}{dt}\right) - \left(\frac{dy}{dt}\right).$$

But

$$\frac{dy}{dt} = \frac{b - q}{L\rho}\left(x - y\right) = \frac{b - q}{bL\rho}\left(L\rho - qt\right)\frac{dx}{dt}.$$

$$\therefore \qquad \left(L\rho - qt\right)\frac{d^2x}{dt^2} = \frac{dx}{dt}\left[b + q - \frac{b - q}{L\rho}\left(L\rho - qt\right)\right]$$

or writing $dx/dt = p$

$$\frac{dp}{p} = \left(\frac{b + q}{L\rho - qt} - \frac{b - q}{L\rho}\right) . dt,$$

which gives

$$\log_e \frac{p}{p_0} = \frac{b + q}{q}\log_e \frac{L\rho}{L\rho - qt} - \frac{b - q}{L\rho} \,.\, t.$$

Now b is large compared with q, and in this case we get

$$\log_e \frac{dx}{dt} = \log_e \frac{bx_0}{L\rho} - \frac{b}{q}\left[\log_e\left(1 - \frac{qt}{L\rho}\right) + \frac{qt}{L\rho}\right].$$

or

$$\frac{dx}{dt} = \frac{bx_0}{L\rho}\left(1 - \frac{qt}{L\rho}\right)^{-\frac{b}{q}} e^{-\frac{bt}{L\rho}}.$$

To simplify this expression, let

$$\alpha = q/L\rho \qquad \beta = b/q.$$

Then

$$dx/dt = \alpha\beta\,(1 - \alpha t)^{-\beta}\; e^{-\alpha\beta t} \,.\, x_0.$$

Substitute

$$1 - \alpha t = z$$

and we get

$$dx = -\,\beta z^{-\beta}\; e^{(z-1)\beta} \,.\, x_0 \,.\, dz.$$

$$\therefore \qquad \int_{x_0}^{x} dx = \beta\, e^{-\beta}\, x_0 \int_{1-\alpha t}^{1} \frac{e^{\beta z}}{z^{\beta}} \,.\, dz.$$

Now

$$\int \frac{e^{ax}}{x^m} \,.\, dx = \frac{e^{ax}}{x}\left[\frac{1}{x^m} + \frac{m}{ax^{m+1}} + \frac{m(m+1)}{a^2x^{m+2}} + \text{etc.}\right].$$

For values of $x < 1$ this series is not convergent, and as $z < 1$, this integration is of no use.

It is accordingly more convenient to calculate the value of dx/dt from the relation

$$\log_{10}\frac{dx}{dt} = \log_{10}\frac{bx_0}{L\rho} - \frac{b}{q}\left[\log_{10}\left(1 - \frac{qt}{L\rho}\right) + M\frac{qt}{L\rho}\right]$$

where M is the modulus for converting natural to common logarithms. If we do this for various values of T, we can then find x by plotting dx/dt against x in the usual way. In this expression the value of b is uncertain, but L, ρ, and q are moderately well known. It is easiest, therefore, to first tabulate the values of

$$\log_{10}\left(1 - \frac{qt}{L\rho}\right) + M\frac{qt}{L\rho}$$

for various values of the time, assuming the values of L, ρ, and q. This is done in Table 1.

TABLE 1.

Time, seconds.	Time, million years.	$\text{Log}_{10}\left(1 - \frac{qt}{L\rho}\right) + M\frac{qt}{L\rho}$.
0	0	0
10^{12}	·03	– ·0000002
1×10^{13}	·32	– ·0000219
2×10^{13}	·63	– ·0000880
3×10^{13}	·95	– ·0001995
4×10^{13}	1·28	– ·0003570
5×10^{13}	1·59	– ·0005617
6×10^{13}	1·90	– ·0008215
7×10^{13}	2·22	– ·0011175
8×10^{13}	2·54	– ·0014687
9×10^{13}	2·85	– ·0018721
1×10^{14}	3·17	– ·0023281
2×10^{14}	6·34	– ·0102
3×10^{14}	9·51	– ·0246
4×10^{14}	12·78	– ·0481
5×10^{14}	15·87	– ·083
6×10^{14}	19·03	– ·137
7×10^{14}	22·19	– ·219
8×10^{14}	25·37	– ·351
9×10^{14}	28·54	– ·545
1×10^{15}	31·72	– ∞

$L\rho = 3 \times 10^2$ calories per c.c.
$q = 3 \times 10^{-13}$ calories per c.c. per second.
t = time in seconds.

It is plain that in the actual problem of the earth's crust, the range of velocity of upward travel of the liquid layer, which is of importance, will be from 1 to 500 km. per million years, or $3{\cdot}17 \times 10^{-9}$ cm., per second, to $1{\cdot}54 \times 10^{-6}$ cm. per second. When such a velocity is attained, the liquid layer will comparatively quickly reach the top of the lower isothermal portion of the crust.

Suppose we take $b = 3 \times 10^{-9}$, which is about half the value we should get if the liquid basalt had the same cooling power as an ordinary mobile liquid.

This gives

$$b/q = 10^4.$$

Furthermore, let

$$x_0 = 1 \text{ cm.}$$

Then

$$\log_{10}\frac{dx}{dt} = \log_{10}\frac{b}{L\rho} - \frac{b}{q}\left[\log\left(1 - \frac{qt}{L\rho}\right) + M\,\frac{qt}{L\rho}\right]$$

or

$$\log_{10}\frac{dx}{dt} = -11 - 10^4\left[\log\left(1 - \frac{qt}{L\rho}\right) + M\,\frac{qt}{L\rho}\right].$$

From Table 1 it appears that the important values of dx/dt will occur between about one million and 1·5 million years. Table 2 shows the values of dx/dt over this range. From these values of dx/dt the value of x has been approximately calculated from the rough approximation that

$$\Delta x = \tfrac{1}{2}(p_1 + p_2)\,\Delta t,$$

where p_1 and p_2 are the values of $\dfrac{dx}{dt}$ at the beginning and end of the interval Δt. Furthermore, the value of $x - y$, the thickness of the melted layer, has been found from the relation

$$x - y = \frac{L\rho - qt}{b} \cdot \frac{dx}{dt},$$

and from this the values of y have also been tabulated.

[TABLE 2.

TABLE 2.

Time. Million yrs.	dx/dt. Km. per 10^6 yrs.	x. Km.	$x - y$. Km.	y. Km.
1·05	·83	·11	·0025	·1075
1·08	1·16	·14	·0036	·1364
1·11	1·74	·19	·0053	·1847
1·14	2·41	·25	·0074	·2426
1·17	3·53	·35	·0108	·3392
1·205	5·20	·48	·0159	·464
1·24	7·8	·69	·0238	·666
1·27	11·7	1·00	·035	·965
1·30	17·9	1·47	·054	1·42
1·33	27·6	2·19	·084	2·11
1·36	43·1	3·31	·13	3·18
1·395	67·6	5·07	·21	4·86
1·43	107·8	7·85	·33	7·52
1·46	173·5	12·31	·52	11·79
1·49	282·5	19·6	·85	18·75
1·52	465·5	31·5	1·41	30·09
1·55	773·	51·1	2·34	48·76
1·585	1300·	84·1	3·93	80·17
1·62	2230·	140·0	6·7	133·3
1·65	3820·	235·	11·4	224·3
1·68	6660·	402·	20·0	382·0
1·71	11800·	693·	35·2	657·8
1·743	20850·	1209·	63·1	1145·9
1·78	37600·	2134·	112·5	2021·5

$L\rho = 3 \times 10^2$.
$q = 3 \times 10^{-13}$.
$b = 3 \times 10^{-9}$.

The table shows how rapidly the upward motion of the melted layer, when once well started, increases; thus at the end of a million years the layer has only moved upwards about ·1 km., while at the end of 1·6 million years it has moved a distance of 100 km.

It is also obvious that the value of b taken cannot be that actually operative

in the case of the earth, since it leads to much too short a period for a thermal cycle, and also to too small a liquid layer, if we assume any reasonable value for the depth of the radio-active basaltic layer.

On these accounts it seems justifiable to conclude that the value of b to be used must be much less than the value I have obtained from the available experimental data. This is not surprising, owing to the fact that basalt has not a very definite melting point, and hence near its melting point its viscosity will be very high, which will have the effect of greatly reducing its cooling power. Let us accordingly assume that $b = 3 \times 10^{-11}$.

This is, of course, a pure assumption; but, as we have really no exact knowledge of the correct value of b, it seems at least interesting to take a value of it which leads to a condition of affairs more closely approximating to that apparently occurring in the earth's history.

TABLE 3.

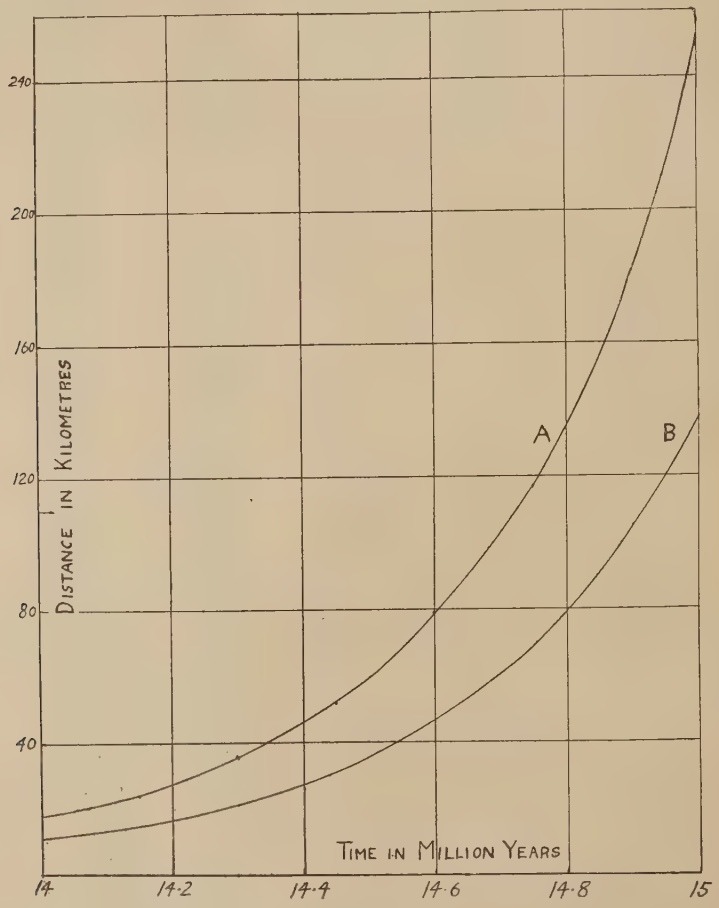
Time. Million yrs.	dx/dt. Km. per 10^6 yrs.	x. Km.	$x - y$. Km.	y. Km.
11·4	·18	·11	·037	·073
11·7	·31	·19	·062	·128
12·05	·57	·33	·112	·218
12·4	1·07	·59	·206	·384
12·7	2·06	1·08	·391	·689
13·0	4·08	2·05	·765	1·285
13·3	8·25	4·00	1·52	2·48
13·6	17·3	8·04	3·12	4·92
13·95	37·1	16·68	6·62	10·06
14·3	83·5	35·7	14·5	21·2
14·6	192·0	79·2	32·8	46·4
14·9	456·	182·	76·6	105·4
15·2	1120·	433·	186·	247·
15·55	2880·	1070·	468·	602·
15·9	7680·	2750·	1220·	1530·

$L\rho = 3 \times 10^2$.
$q = 3 \times 10^{-13}$.
$b = 3 \times 10^{-11}$.

Table 3 shows the values now obtained for the various quantities. They agree much better with the usually accepted values for the time between two

successive revolutions in the earth's history, although they are still probably too low. The discrepancy would, however, be reduced if we took into account that for the lower strata the value of q may be decidedly smaller than 3×10^{-13}.

This is, as a matter of fact, rather supported by the available measurements on the radio-activity of the eclogites and other rocks of probable deep-seated origin.



GRAPH 1.

I have plotted the results in the graph shown. The upper curve, marked "A," indicates the distance the upper surface of the liquid portion will have travelled upwards in the time shown along the horizontal axis, while the lower curve B shows the distance moved by the lower surface of the liquid portion.

The distance between the two curves thus gives the depth of the liquid at any time. Thus, suppose we assume that the total height of the radio-active column is 151·5 km., we find that the depth at which the melting point, taken to be 1000° C. over the surface temperature, would be obtained is 51·5 km. The depth of the thermally isolated portion is accordingly 100 km., and if our premises are taken it will be seen that at the end of about 14·7 million years the upper surface of the liquid substratum will have reached the bottom of the portion of the crust which is in thermal equilibrium with its own heat supply, and that the depth of the liquid will then be about 43 km.

There are two obvious objections to these conclusions. In obtaining them I have assumed (*a*) a liquid layer 1 cm. thick at the base of the column at zero time, and (*b*) the rest of the column up to the equilibrium height everywhere originally at its melting point, but entirely solid. Objections can be urged against both of these. It will be seen, however, that $\frac{dx}{dt}$ is simply proportional to the thickness x_0 of the original layer. From Table 3 we see that if x_0 were taken only as 1 mm., it would only increase the period to about 15·5 million years, a step, as a matter of fact, in the right direction. As regards the second assumption, it is undoubtedly correct for the larger portion of the column, since once the melted layer has attained any appreciable thickness it moves up so rapidly that the time of its motion may be neglected compared with the time between two successive revolutions. This is not true for the lowest levels, where the motion is slow, but the error introduced will only be a quantitative one; and, as all our quantities are already so uncertain, this extra small uncertainty is not really of much importance. It will ensure, however, that melting will first take place in the lower layers.

We might have started with the assumption that it took a certain definite time for the melted layer at the base of the column to be formed. During this time a certain percentage of the upper layers will have melted. It is found that this really is equivalent to reducing the effective value of the latent heat in our equations. The time of a revolution will then be the time required to form the initial layer, plus the time required for the layer to move upwards in the material with this reduced latent heat. This time will be greater than the figures I have calculated on the original premises. Its value will depend on the time we assume is required to form the initial basal melted layer.

Disregarding these possibilities, let us revert to the consideration of the future history of the original postulated system. The condition of affairs at the end of the first state of the thermal cycle is depicted in fig. 4. The upper 51·5 km. of the crust is solid, and in thermal equilibrium with its own radio-active heat supply. Underneath this lies a layer of liquid, 43 km. thick, and this will now proceed to melt its way up through the overlying solid, gradually becoming thinner in doing so, till it finally disappears. This is the second stage of the revolution, and it is now proposed to attempt to make some rough estimate of the probable course of events in its evolution.

The two equations that govern the system now are, as already stated:

$$L\rho \cdot \frac{dx}{dt} = b(x - y) - Kf(h, t)$$

$$L\rho \cdot \frac{dy}{dt} = (b - q)(x - y),$$

where $f(h,t)$ is the temperature gradient at the lower surface of the upper solid crust. It is not possible to solve these equations unless we can express $f(h,t)$ in terms of x, y, and t, and this I have not succeeded in doing. As a rough approximation, I first adopted the hypothesis that the value of $f(h,t)$ would be sensibly the same as that in a radio-active crust of thickness h, with its lower surface at the melting point, but kept in thermal equilibrium, so that no actual melting would occur. If the motion upwards of the liquid layer were sufficiently slow, this approximation would be fairly correct. However, I found that the upward velocity was too great. It leads to the layer of liquid moving upwards with practically undiminished thickness till the crust is reduced to about 0·5 km. This conclusion is obviously incorrect, as the increase of thermal energy in the solid portions of the crust would in this case demand a large diminution in the liquid layer to supply it, quite apart from any loss of energy due to conduction at the surface.

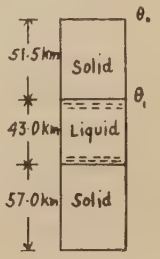


Fig. 4.

In our assumption of the maintenance of the equilibrium gradient we neglect entirely the part of the heat flow required to attain the equilibrium state. It is only when the layer moves up excessively slowly, so that the heat lost by conduction is large compared with the heat required to heat up the upper solid, that this will be approximately correct. This calculation has thus shown that in the case under consideration this assumption is not justifiable.

The problem has accordingly been attacked in a slightly different manner. I have assumed that at any time the distribution of temperature in the solid layer is approximately the equilibrium one, but I have only used this assumption to calculate the surface gradient and the total thermal energy of the layer. At first sight this might appear to lead to the same results as before, but such is not the case. It is plain that while the gradient just over the melted layer may differ very largely from the equilibrium gradient, the actual average

temperature of the whole layer, since its lower and upper temperatures are fixed, will never differ very largely from that calculated from the equilibrium distribution. The surface gradient also will be more nearly the equilibrium one, since it is not directly affected by the heat flow necessary to heat up the crust.

Let fig. 5 represent the state of affairs at any time.

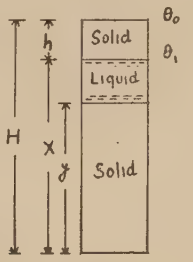


Fig 5.

The temperature in upper solid at depth z is given

$$\theta = \theta_0 + az - \frac{qz^2}{2K}$$

when $z = h \quad \theta = \theta_1$, the melting point.

Also $a = \dfrac{d\theta}{dz}$ when $z = 0$.

Let E = total heat energy in column,

s = specific heat.

Then
$$E = \rho s \int_0^h \theta \, . \, dz + \rho s \theta_1 \, . \, x + L\rho(x - y)$$

$$= \rho s \left[\theta_1 x + \int_0^h \left(\theta_0 + az - \frac{qz^2}{2K} \right) dz \right] + L\rho(x - y)$$

$$= \rho s \left[\theta_1 x + \theta_0 h + \frac{ah^2}{2} - \frac{qh^3}{6K} \right] + L\rho(x - y)$$

But
$$a = \frac{\theta_1 - \theta_0}{h} + \frac{qh}{2K}.$$

$\therefore$
$$E = \rho s \left[\theta_1 x + \theta_0 h + \frac{h(\theta_1 - \theta_0)}{2} + \frac{qh^3}{12K} \right] + L\rho(x - y)$$

$$= \rho s \left[\theta_1 H - \tfrac{1}{2}(\theta_1 - \theta_0)h + \frac{qh^3}{12K} \right] + L\rho(x - y).$$

Or writing $H - x$ for h

we have $$E = \rho s\left[\theta_1 H - \tfrac{1}{2}(\theta_1 - \theta_0)(H - x) + \frac{q(H-x)^3}{12K}\right] + L\rho(x - y).$$

$$\therefore \quad \frac{dE}{dt} = \rho s\left[\tfrac{1}{2}(\theta_1 - \theta_0) - \frac{q(H-x)^2}{4K}\right]\frac{dx}{dt} + L\rho \cdot \frac{d}{dt}(x - y).$$

Now, the rate of gain of energy of the column due to radio-active heating is $q(h + x - y)$. The radio-activity of the lower solid layer does not enter our equations, since it only produces a very slow partial melting of this layer, and in calculating the total thermal energy of the column we have neglected it.

Again, the rate of loss of heat at the surface $= Ka$. Hence the net rate of gain of heat due to these two causes $= q(h + x - y) - Ka$. This must be equal to $\frac{dE}{dt}$;

$$\therefore\ q(h + x - y) - Ka = \rho s\left[\tfrac{1}{2}(\theta_1 - \theta_0) - \frac{qh^2}{4K}\right]\frac{dx}{dt} + L\rho \cdot \frac{d}{dt}(x - y),$$

Now,

$$Ka - qh = \frac{K(\theta_1 - \theta_0)}{h} - \frac{qh}{2}$$

$$= KA$$

where

$$A = \frac{\theta_1 - \theta_0}{h} - \frac{qh}{2K};$$

$$\therefore\ \frac{\rho sh}{2}\left[\frac{\theta_1 - \theta_0}{h} - \frac{qh}{2K}\right]\frac{dx}{dt} + KA - q(x - y) + L\rho \cdot \frac{d}{dt}(x - y) = 0.$$

Or, finally, since

$$L\rho \cdot \frac{dy}{dt} = (b - q)(x - y)$$

$$\frac{dx}{dt}\left[L\rho + \frac{\rho sh}{2} \cdot A\right] = b(x - y) - KA.$$

The method adopted for very roughly solving this equation is as follows:— The quantity $L\rho + \frac{1}{2}\rho sh \cdot A$ can be calculated for any value of h. The value taken for the specific heat is 0·3 calorie per g., about that of basalt. Suppose that when $h = h_1$ the value of $x_1 - y_1$ is known. We can now obtain the upward velocity of the top of the liquid layer, say v_1, from the relation

$$v_1 = \frac{dx_1}{dt}$$

$$= \frac{b(x_1 - y_1) - KA_1}{L\rho + \frac{1}{2}\rho sh_1 A_1}$$

Let us now consider the condition of affairs when the crust has decreased to a thickness h_2. If $h_1 - h_2$ is not too large, we may neglect the change in $x - y$ in calculating v_2—

$$v_2 = \frac{b(x_1 - y_1) - KA_2}{L\rho + \frac{1}{2}\rho s h_2 \cdot A_2}.$$

The average velocity during the interval will be approximately $\frac{1}{2}(v_1 + v_2)$, and hence the time Δt that is required for this change to take place is given by

$$\Delta t = \frac{2(h_1 - h_2)}{v_1 + v_2}.$$

Let $\Delta(x - y)$ be the actual small change in the value of $x - y$. The original thermal energy in the column is

$$E_1 = \rho s\left[\theta_1 H - \tfrac{1}{2}(\theta_1 - \theta_0)h_1 + \frac{q h_1^3}{12K}\right] + L\rho(x_1 - y_1).$$

Hence the gain in energy will be

$$E_2 - E_1 = \rho s\left[\tfrac{1}{2}(\theta_1 - \theta_0)(h_1 - h_2) - \frac{q}{12K}\left(h_1^3 - h_2^3\right)\right] + L\rho\Delta(x - y).$$

The amount of heat generated, however, may be taken as $q(h_2 + x_1 - y_1)\Delta t$, but from this we must subtract the heat lost at the upper surface. This is equal to $Ka\Delta t$, where a is the mean surface gradient during the interval. We thus have

$$E_2 - E_1 = [q(h_2 + x_1 - y_1) - Ka]\,\Delta t,$$

which finally gives

$$-L\rho\Delta(x - y) = \rho s\left[\tfrac{1}{2}(\theta_1 - \theta_0)(h_1 - h_2) - \frac{q}{12K}\left(h_1^3 - h_2^3\right)\right] + [Ka - q(h_2 + x_1 - y_1)]\,\Delta t.$$

$\Delta(x - y)$ is essentially a negative quantity, since the layer steadily diminishes in thickness throughout practically the whole period. Thus $\Delta(x - y)$ can be calculated. The new thickness of the layer is obtained by subtracting $\Delta(x - y)$ from the original value, and the process repeated, assuming that this new thickness remains constant while moving from h_2 to h_3, and so on. By this method the values given in Table 4 have been obtained. The time is reckoned from the commencement of the second stage. When $b(x - y) = KA$, the upward velocity becomes zero, and thus for small values of $b(x - y) = KA$ the method adopted is not very suitable. It was found that $b(x - y) = KA$ when $h = 8{\cdot}25$ km.

TABLE 4.

Time in million years.	Thickness of upper solid layer in km.	Thickness of liquid layer in km.
0·00	51·5	43·0
0·01	50·0	43·0
0·06	45·0	41·9
0·11	40·0	39·6
0·18	35·0	36·1
0·26	30·0	31·6
0·35	25·0	26·3
0·47	20·0	20·2
0·64	15·0	13·4
0·78	12·0	8·9
0·93	10·0	5·5
1·07	9·0	3·5
1·20	8·5	2·2
1·35	8·25	1·1
1·57	—	0·0

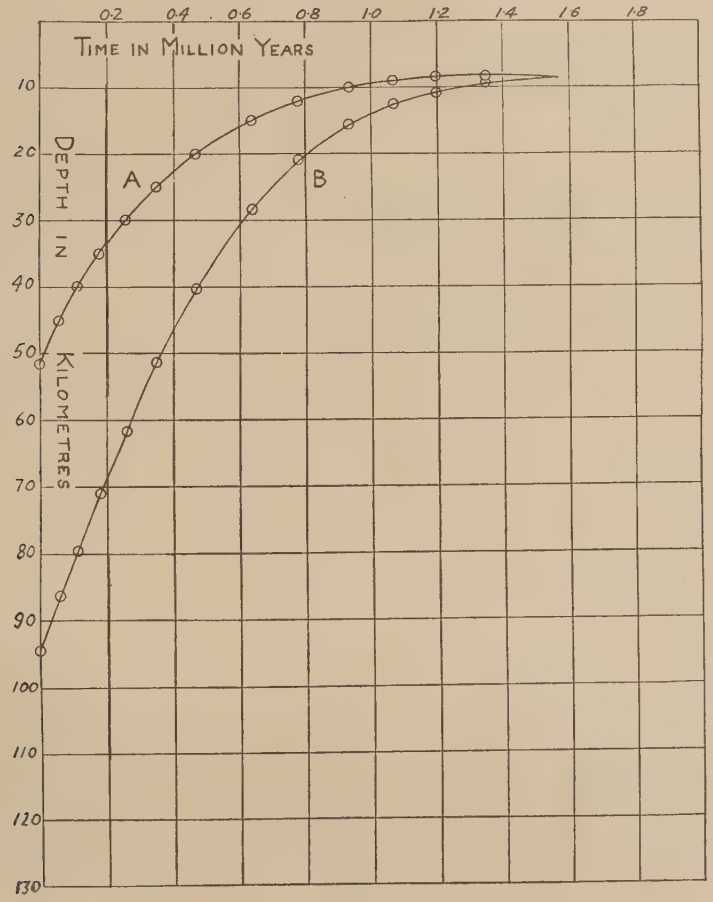
The extra time required to completely solidify the layer at this depth was then given by

$$K\Delta t\left[\frac{\theta_1-\theta_0}{h}+\frac{qh}{2K}\right]=L\rho\,(x-y),$$

e.g., the time required to solidify a layer 1·1 km. thick at a depth of 8·25 km. is 0·22 million years. In this we assume that when the loss of heat through the upper solid becomes greater than the heat brought up by convection, still that the solid produced at the top of the layer falls to the bottom, and does not collect on the upper layer and thicken it. As the depth of the layer is small compared with the thickness of the upper solid, the error, if any, introduced by this assumption will, however, be small.

I have plotted the values given in Table 4 in Graph 2. The time in million years is plotted horizontally, and the depth in kilometres vertically. Curve A

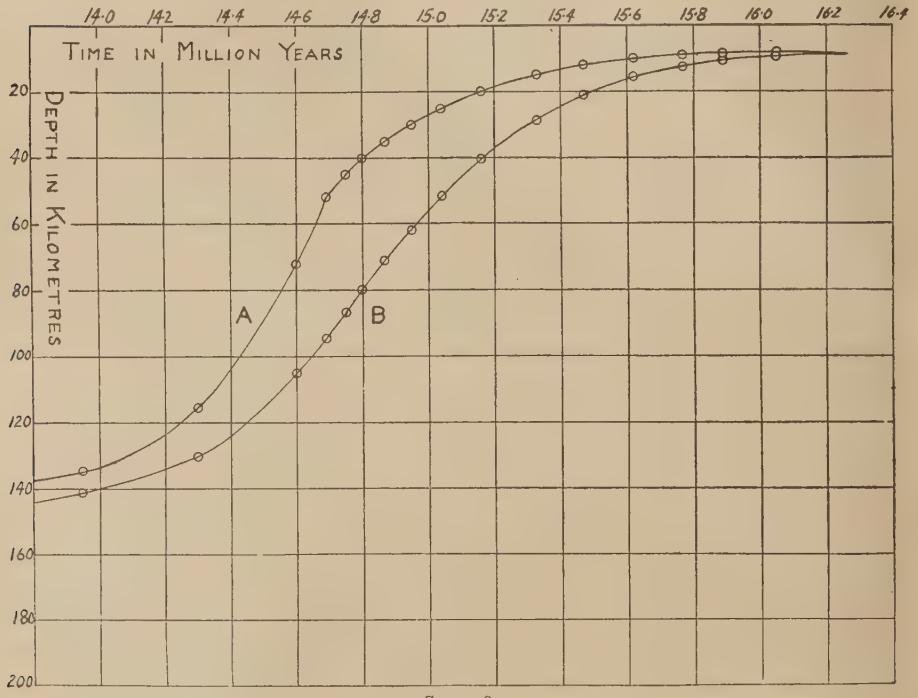
shows the position of the upper surface of the melted layer, and B that of the lower surface. The graph shows very well the rise of the liquid layer, and also its diminution in thickness as time progresses. In Graph 3 the whole history of the first melting of the column is illustrated by combining the results of Tables 3 and 4.



GRAPH 2.

The first stage when melting occurs below the melting point geotherm takes about 14·7 million years. In this stage the melted layer moves upwards with rapidly increasing velocity and thickness. When the level of the melting point geotherm is reached, the commencement of loss of heat by conduction through the upper solid introduces a sudden change in the conditions. The

discontinuity in the Curve A at this point is due to this fact. In the second stage the layer continues to move up, but with steadily decreasing velocity and thickness. The minimum value the upper crust ever attains is about 8·25 km., and the time taken from the commencement of the whole cycle till the melted layer finally disappears is about 16·25 million years.



GRAPH 3.

At the end of the first cycle we are left with the column again nearly entirely solid, but the melting point geotherm only at a distance of 8·25 km. below the upper surface. Below this the solid is everywhere at its melting point, and gradually remelting. As time progresses the melting point geotherm will gradually fall, due to loss of heat in the upper levels by conduction. This process continues until the new melted layer rising from below meets the melting point geotherm, which it then carries with it to comparatively near the surface again, the melted layer itself gradually disappearing in this process.

It is difficult to determine the exact history of the second thermal cycle. This arises from the fact that in the lower layers the initial conditions are rather uncertain. We cannot without further consideration assume that at the beginning of the cycle we have a liquid layer 1 cm. thick at the base of the column, and thus the exact course of the remelting of the column below the

melting point geotherm is rather uncertain. It seems possible, however, that by considering the small inflow of heat from a lower infusible layer, such as probably occurs in the earth's crust, we may be able to remove this objection. Neglecting this complication, and taking that the remelting of the lower column in the second case takes about the same time as in the first, we can arrive at some rather interesting results.

Since the melting point geotherm starts near the surface, it will steadily sink during the first stage of the thermal cycle. J. R. Cotter (Phil. Mag., Sept., 1924) has shown how the fall of the melting point geotherm may be calculated on certain grounds. The method is, however, rather laborious, and I have adopted an alternative method.

If the geotherm falls from a depth h_1 to a depth h_2 in a time Δt, we have that the loss of heat at the surface equals the radio-active energy generated in the layer, plus the loss of thermal energy of the upper crust. In calculating the latter we have to remember that the portion of the crust $h_2 - h_1$ will not be entirely solid, but will be partially melted. If t is the time from the commencement of the thermal cycle, when the whole crust was all practically solid simultaneously, the amount of energy stored up as latent heat of fusion will be approximately $qt(h_2 - h_1)$.

Our equation then is

$$(Ka - qh_2)\,\Delta t = E_1 - E_2 + qt\,(h_2 - h_1),$$

where a = the average surface gradient.

$E_1 - E_2$ = loss of thermal energy of crust due to cooling.

$qt\,(h_2 - h_1)$ = loss of energy due to resolidification.

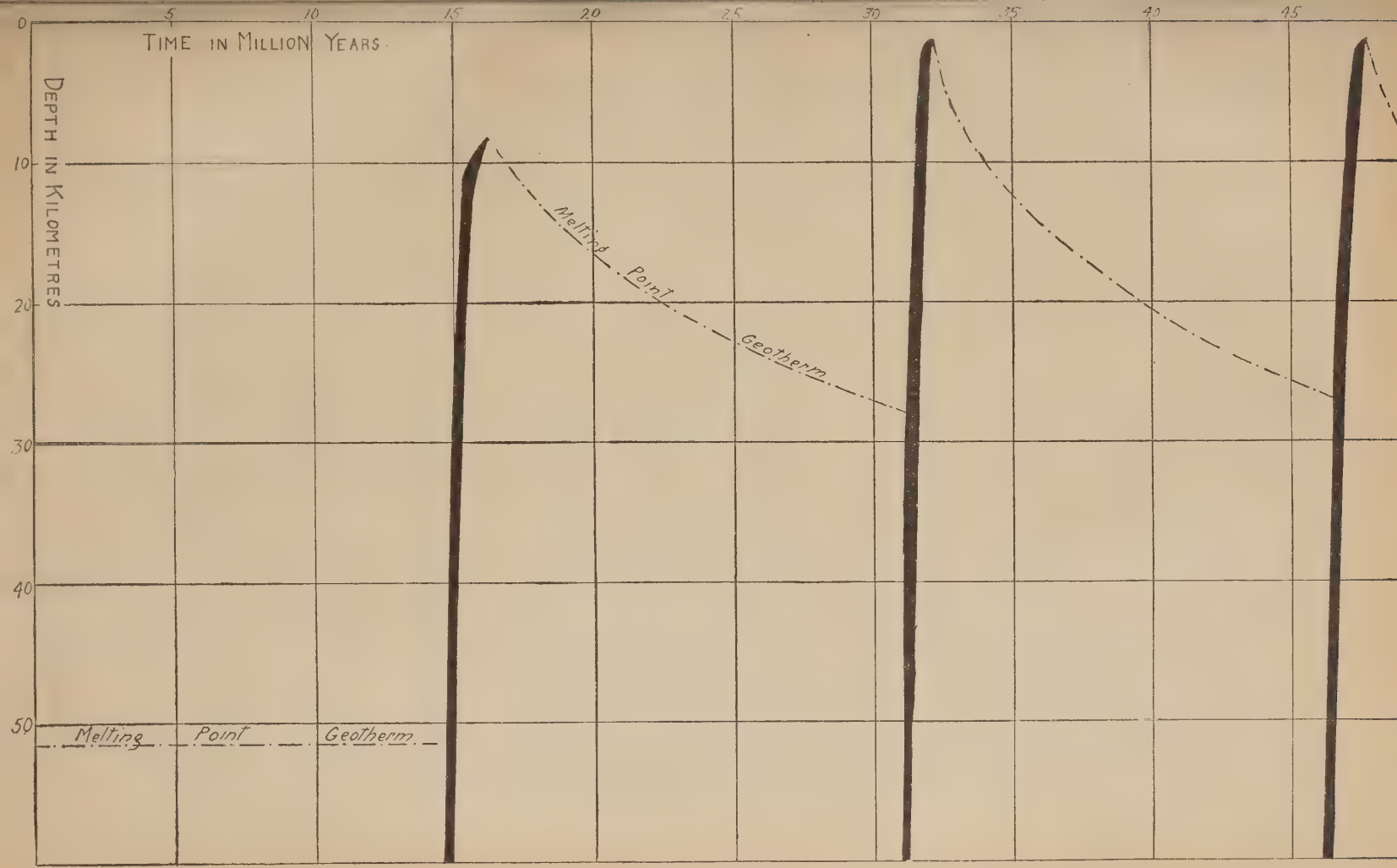
Taking $h_1 - h_2$ not too large, we can calculate a roughly, and hence solve for Δt. By repeating this process, Table 5, showing the fall of the geotherm, has been obtained. It will be seen that in fifteen million years the geotherm has sunk to approximately 28 km. depth. It will then meet the melted layer rising from below, which will, however, in this case be about 52 km. thick instead of 43 km., since it has travelled upwards an additional 23·5 km. before meeting the melting point geotherm.

[TABLE 5.

TABLE 5.

Depth of melting point geotherm in km.	Time in million years.
8·25	0·0
8·5	·075
9·0	·25
10·0	·61
12·0	1·41
15·0	2·91
20·0	6·26
25·0	11·0
30·0	18·0
35·0	28·1

By the method already described, it is possible to trace the rise of this liquid to the surface. Owing to the fact that the layer is thicker, and starts closer to the surface, it is found that the minimum thickness of the crust is now only about 1·2 km. In Graph 4 I have shown the approximate history of the first three thermal cycles. After the first cycle it is found that the minimum thickness of the crust remains practically constant. The period is about sixteen million years. The black, nearly vertical, bands on the graph show the rise of the liquid layer. The upper edge of the band shows the position of the top of the liquid, and its lower edge that of the bottom. The position of the melting point geotherm in the intervals between fusions is given by the chain dotted curve.


TIME IN MILLION YEARS
DEPTH IN KILOMETRES
0
5
10
15
20
25
30
35
40
45
10
20
30
40
50
Melting Point
Geotherm
Melting Point
Geotherm

GRAPH 4.

As regards the bearing of the results obtained on the actual history of the earth's crust, there are many different considerations to be taken into account. Firstly, the period of revolution I have obtained is much shorter than that usually estimated. This discrepancy may be partially due to the assumed value of q being too high. The results show clearly that it is the radio-activity of the column below the equilibrium position of the melting point geotherm that mainly controls the period of a thermal cycle.

It is now widely held, however, that at these depths the earth's crust is eclogitic in nature. Surface eclogites are found to be only about half as radio-active as normal plateau basalts, and accordingly it would seem that q for the lower layers cannot be greater than $1{\cdot}5 \times 10^{-13}$ cals. per c.c. per second, and is probably considerably less. This consideration would have the effect of increasing the period of a thermal cycle by a factor of at least two, and probably more. Furthermore, the value of b is purely an assumed one, and until we can obtain some further experimental data as to the rate of transference of heat from a liquid to its own solid, and the effect of the viscosity of the liquid on this rate, it will have to remain so. In a general way, decreasing the value of b increases the period of the thermal cycle and the magnitude of each remelting.

In conclusion, I should wish clearly to point out that my results only refer to a crystalline crust. When we come to deal with the actual crust, which melts in a rather indeterminate manner, it becomes very difficult to say what we precisely mean by the melting point gradient and the adiabatic gradient. Pending further investigation on these points, it would be premature to claim that the occurrence of thermal cycles in the earth's crust can be indisputably demonstrated theoretically; but at least it would appear that their occurrence would not be contrary to any of the laws of heat, and that, in order to explain the nearly completely solid condition of the earth at certain periods, it is not necessary to assume that it contains less radio-active matter than that required to supply its present heat loss at the surface.

No. 33.

STUDY OF THE POLYSACCHARIDES.

Part I.—Inulin and Inulan.

By J. REILLY and P. P. DONOVAN, M.Sc.,
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[Read June 25, 1929. Published separately February 22, 1930.]

The study of the molecular constitution of the polysaccharides (which includes starch, cellulose, dextrin, inulin, glycogen, manna, lichenin, and xylan) presents many difficulties, due to their high molecular weights, amorphous character, sparing solubility in water, tendency to easy polymerisation, and lack of well-defined derivatives.

These complex substances are now generally considered to be the result of the polymerisation of a particular fundamental unit for each polysaccharide. As regards the nature of this polymerisation, different views are held, and the position is clearly summarised in Haworth's Constitution of Sugars (pp. 74–96).

The aggregation of the fundamental unit may be considered (cf. Hess, Annalen, 1923, **435**, 116, and Pringsheim Ber., 1926, **59**, 3008) to take place by the exercise of co-ordinate co-valencies, in which the aggregate molecule may revert to the original unit by being subjected to a variety of external conditions. The other view holds that the aggregation is not due to any exercise of residual valencies, but to ordinary structural change, in which the structural unit is thought to be linked up by connecting the oxygen atoms of the anhydro ring in a chain of indefinite length by ordinary valency (cf. Haworth and Learner, J.C.S., 1928, 621).

In the present work the authors have studied the de-polymerisation of inulin under controlled conditions, with the possible formation of a unit. The discussion as to the identity of this unit may be considered to centre round three main ideas. One view indicates that the unit is a λ-anhydro-fructose molecule, which polymerises by structural valency (cf. Haworth and co-workers, *ibid.*, and J.C.S., 1928, 2690). The second view indicates that the fundamental unit may be a di-fructose anhydride—$(C_6H_{10}O_5)_2$—and that the aggregation is then formed by the exercise of the co-ordinate co-valency of the oxygen atoms

of the oxide rings in co-ordination with the hydrogen atoms of the hydroxyl groups. A third view, developed by Hess with regard to cellulose (Annalen, 1923, **435**, 116), and which may be applied generally to the polysaccharides, would be that the structural unit of inulin is a λ-anhydro-fructose molecule, and that the aggregation takes place by means of the operation of co-ordinate co-valencies, in which the oxygens of the two oxide rings in the fructose anhydride molecule are co-ordinated with the hydrogen atoms of the two hydroxyl groups.

When inulin acetate is heated in chloroform solution with a small amount of benzene-sulphonic acid for a number of hours depolymerisation occurs (Pringsheim and Reilly, Ber., 1928, **61**, 2018). The regenerated polysaccharide from the acetate closely resembles inulin, and has the same specific rotation. It is, however, more soluble in water, and the molecular weight in water indicates a formula $(C_6H_{10}O_5)_2$. Whether this is the structural unit of inulin has yet to be proved; but, to prevent any confusion, this product will not be called inulin, but inulan. The molecular weight of inulin in liquid ammonia (Schmid and Becker, Ber., 1925, **58**, 1968) also corresponds to $(C_6H_{10}O_5)_2$, but this molecule of low molecular weight was not isolated from the ammonia. The authors have now endeavoured to isolate the structural unit of inulin by directly "breaking down" the high aggregate molecule. They have made the important observation that inulin is soluble in acetamide, and the nature of the complexity of the molecule is found to be influenced by solution in such solvent, and a short account of the work has been published (Pringsheim, Reilly, and Donovan, Ber., 1929, **62**, 2378). The molecular weight of inulin in acetamide has been determined cryoscopically, with interesting results. At various concentrations a molecular weight was arrived at corresponding to $(C_6H_{10}O_5)_2$, which agrees with the suggestion of a "di-mer unit." This lower polymer inulan was recovered from acetamide by dissolving inulin in molten acetamide and keeping the temperature at 90° C. for about 2 hours, and then throwing out the inulan by addition of absolute alcohol.

The molecular weight of the inulan was then determined by depression of freezing point of water. Values were again obtained corresponding, not with the original inulin, but with the polysaccharide aggregate reduced in complexity, giving an inulan molecule of $(C_6H_{10}O_5)_2$. The di-mer was dissolved in water and thrown out with alcohol. After a period of one month the molecular weight of this product was again determined in water, and values were now obtained corresponding to the large aggregate molecules of $(C_6H_{10}O_5)_{15}$ and $(C_6H_{10}O_5)_{16}$. Inulin which had been purified by dissolving in water and recovery with alcohol gave a molecular weight determination in water values corresponding to $(C_6H_{10}O_5)_7$ and $(C_6H_{10}O_5)_8$.

On determining the specific rotary power of inulan and the high aggregate inulin molecules, an identical result was obtained in each case (Pringsheim, Reilly, and Donovan, Ber., *ibid.*). The results arrived at in this work point to the view that the structural unit of inulin may be the di-fructose anhydride

molecule $(C_6H_{10}O_5)_2$. It seems probable that the di-mer anhydride is linked up internally by ordinary structural valency, and that the aggregate molecule is then formed by the exercise of the co-ordinate co-valencies of the oxygen atoms in co-ordinating with the hydrogen atoms of the hydroxyl groups. The fact that the specific rotary power is identical in each case points strongly to the conclusion that the aggregation is not due to an open chain structural linking —which would be expected to introduce a constitutive effect—but rather to the residual valency linking.

The phenomenon of quick polymerisation also points strongly to the loose linking of the units. An objection to the suggested di-mer unit may be that odd values of such as $(C_6H_{10}O_5)_7$ and $(C_6H_{10}O_5)_9$ have been found. This, however, is probably due to mean molecular weights of different aggregations of the possible unit in the solvent.

The reducing power of inulin has been attributed to the terminal reducing groups of the open chain of anhydro-fructose units (Drew and Haworth, J.C.S., 1928, 2690). In view, however, of the fact that even highly purified cane sugar, which has no terminal reducing groups, also shows small and progressive reducing power, this experimental evidence regarding the reducing power of inulin cannot be considered as conclusive in proof of the existence of terminal reducing groups in inulin. In addition to the reducing figures for inulin and cane sugar, the corresponding figures for inulan and laevulosan (Pictet and Reilly, Helvetia Chimica Acta, 1921, **4**, 613) were determined. In the diagram are given the comparative reduction powers of the four carbohydrates.

Experimental.

The following was the method of purification of commercial inulin. The inulin was dissolved in boiling water, the solution filtered, and the inulin frozen out by immersing the solution in ice.

The separated inulin was again dissolved and re-frozen out. It was then dissolved in boiling water, and thrown out with absolute alcohol. The precipitate was allowed to stand for several hours and then filtered. This process was repeated three times. The inulin thus purified was quite white, and the ash content 0·05 %. $[\alpha]^{20} = -31{\cdot}2°$ in water.

Inulin was also extracted from artichokes by boiling with water, filtering, and precipitating with alcohol. The inulin, after charcoal purification, was again dissolved in boiling water, filtered, and re-precipitated with alcohol. This operation was repeated three times.

No difference was observed between the different samples of purified inulin.

Some inulin was then dried in a vacuum at 70° C., and its molecular weight determined by the depression of the freezing point of acetamide.

The acetamide was purified by crystallising from chloroform and dried in vacuum at 50° C.

Molecular Weight of Inulin in Acetamide.

Substance. (g.)	Acetamide. (g.)	Conc. in %.	Depression.	Mol. Wt.
0·25	10	2·5	0·301°	301
0·10	12	0·83	0·092°	329

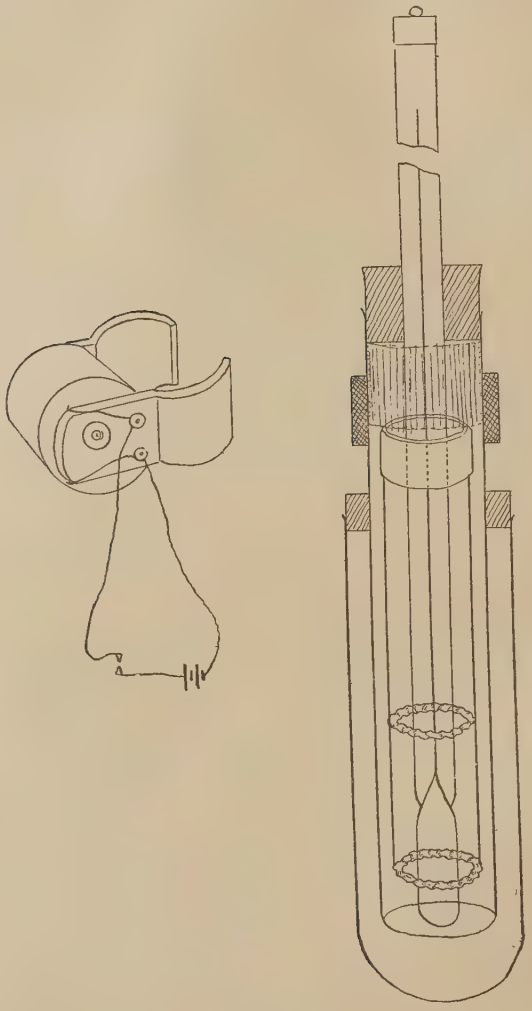

Fig. 1.

On account of the hygroscopic nature of acetamide, a closed apparatus was employed for the molecular weight determinations. In the experiment the

stirring of the solvent and solution was effected by means of an electro-magnetic device. The liquid was stirred in a closed tube by a platinum stirrer, with iron top, which was lifted by a solenoid round the top of the tube, which was connected to a "make and break" attached to two secondary cells. In fig. 1 the front view of the solenoid round the tube containing the thermometer, solution, and stirrer is shown, and the side view shows the solenoid attached to the "make and break" and cells.

This lower polymer of inulin, known as inulan, was extracted from acetamide by the following method:—About 3 grams of inulin were dissolved in 150 grams of molten acetamide for about 2 hours. (These weights were taken so as to approximately coincide with the weights taken in the molecular weight determinations, though subsequent experiments showed that greater proportions of inulin might be taken with the same results.) Absolute alcohol was then added, and the polysaccharide precipitated. The substance was dried at 70° C. in a vacuum, and its molecular weight determined by the depression of freezing point in water.

Substance. (g.)	Water. (g.)	Conc. in %.	Depression.	Mol. Wt.
0·25	30	0·83	0·05°	310
0·32	30	1·06	0·06°	331

The molecular weight of the air-dried inulan (after solution in water) was again determined in water after a period of four months, and the following example illustrates the results obtained:—

Substance. (g.)	Water. (g.)	Conc. in %.	Depression.	Mol. Wt.
0·8	30	2·6	0·02°	2480

The molecular weight of inulin in water was again determined in a similar manner, and gave values of n ranging between 7 and 8.

Substance. (g.)	Water. (g.)	Conc. in %.	Depression.	Mol. Wt.
0·5	30	1·6	0·025°	1240

The reducing powers of inulin, inulan, laevulosan, and cane sugar, after heating in water for progressive periods, were then estimated by boiling with Fehling's solution for three minutes and filtering.

The precipitated cuprous oxide in the Gooch crucible was washed with boiling water, alcohol, and ether, and dried at a temperature of 100° C. before weighing. The reducing power was also estimated by the following volumetric method, and there was a close agreement in each case between the weights of cuprous oxide determined, gravimetrically and volumetrically. The precipitated cuprous

oxide in the crucible was dissolved with a little nitric acid, and washed through with boiling distilled water into a conical flask. The acid solution was neutralised by adding solid sodium carbonate till a precipitate formed; this was dissolved with a little acetic acid, and a few grams of solid potassium iodide added. The liberated iodine was then titrated with N/10 thiosulphate. From this the amount of cuprous oxide can be calculated. The comparison of inulin, inulan, laevulosan,

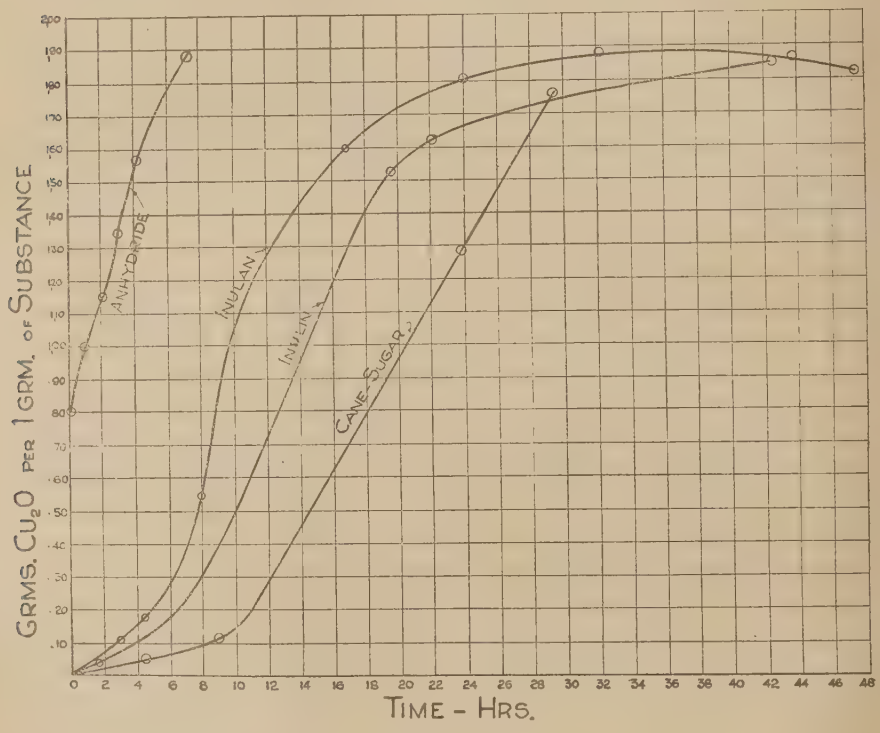

Fig. 2.

and cane sugar is shown in fig. 2. When reduction was completed, the resulting solutions from inulin, inulan, and laevulosan were examined, and an osazone prepared in each case. These were shown to be similar (M.P. 206°), agreeing with that of the osazone from fructose.

This work is being extended to other polysaccharides, and the results of solution of lichenin, xylan, glycogen, and starch in acetamide are now being examined.

34

RESPONSES OF PLANT-TISSUES TO ELECTRIC CURRENTS.—II.

By H. H. DIXON, Sc.D., F.R.S.,
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AND
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[Read January 28. Published separately April 4, 1930.]

This paper contains a short account of some experimental work carried out with a view to ascertaining how far the results previously obtained with leaf-tissues of *Hedera helix* and *Sedum praealtum* (Dixon and Bennet-Clark, 2) resemble those given by other tissues, and especially to find out if small groups of cells, or single cells, behave in a manner similar to massive tissues.

As in earlier work, it was found that the presence of conducting films of solutions over the outside surfaces of wettable tissues precludes the use of portions excised from surrounding masses. This renders the filaments of algae unsuitable as subjects for experiment. Cell groups had to be found, of which the surfaces not in contact with the electrodes retained a natural waterproof covering.

Series of experiments were carried out with filaments of the stamens of *Acacia dealbata*, with the staminal hairs of Tradescantia spp., and with pressed yeast.

Each Acacia stamen is about 7·5 mm. long, and about 0·04 mm. in diameter. It is traversed by a very fine axial vascular bundle, and round this the greater part of the filament is formed of relatively large cells at the proximal end of the stamen, and progressively smaller ones as the distal end is approached.

About 15 to 25 of these cortical cells appear in each transverse section, and about 20 to 30 cells occur in each longitudinal column 5 mm. long.

Two platinum black electrodes were loaded, each with a drop of Knop's solution, and a piece of a filament 5 mm. long, with a fresh-cut surface at each end, was arranged to span the space between the drops.

The currents used, both for the measurement of the conductivity and for stimulation, thus had to pass a conductor consisting of about 20 chains of about 30 cells each.

The resistance of this conductor was so great that its measurement by means of the Kohlrausch bridge was impracticable, and, instead, the measurements were made by means of a high resistance galvanometer. This galvanometer gave

a deflection of 1 mm. on a scale at a distance of one metre with a current of $2{\cdot}5 \times 10^{-9}$ amps.

In setting up the circuit, it was arranged by means of a key that the measuring current might be passed in either direction through the stamen, while it passed through the galvanometer always in the same direction; hence, with either direct or reversed current through the stamen, the deflection of the galvanometer was always in the same direction.

A known pressure of 0·2 to 1·0 volt was obtained from a small accumulator and potentiometer. From this voltage and the current flowing, as measured by the galvanometer, the resistance of the stamen was calculated.

It was expected that the effect of polarisation at the membranes in the tissue on the apparent resistance might be avoided by rapid reversals of the direction of the current through the tissue, the current passing through the galvanometer always in the same direction.

This was not possible in practice, for the rather curious reason that the deflection in the galvanometer was greater when the current passed through the tissue in one direction than in the opposite direction.

This difference in galvanometer deflections was far greater than the deflection obtained when the ends of the stamen were connected to the galvanometer directly, in which case a small deflection of 1–2 mm. was observed. When a pressure of 1 volt was applied to the circuit, a deflection of the order of 30 mm. was observed when the current passed in one direction through the tissue, but when the current flowed in the opposite direction a deflection of about 40–50 mm. was obtained.

The tissue thus acts as a rectifier. Differences in permeability, which might account for this rectifying action, have been observed in asymmetric membranes, such as seed-coats (Brauner, private communication, and Denny, 1), and the frog skin (Hamburger, 4), by means of other methods in addition to the electrical conductivity.

This differential permeability renders the measurement of the conductivity somewhat difficult, especially as the galvanometer was not critically damped; the method employed was to allow the galvanometer mirror to swing, and observe the slow return towards zero. The reading at the first lag in this return to the zero point was taken to represent the current flowing before polarisation commenced; this lag was followed by a steady decrease of the deflection as polarisation proceeded.

The application of a stimulus of, say, 50 volts (A.C. 50 cycles) for 1 second caused the resistance to fall rapidly to about 60 per cent. of its original value. The resistance continued to fall after the stimulating current had ceased, as had been observed before when the leaves of Hedera and Sedum were used. After some time it rose again from the minimum value.

The differences between the currents in opposite directions, which existed before the stimulus, were in some cases increased after the stimulus, in other cases

they were decreased, or even reversed. Inasmuch as alternating current stimuli were used, this very variable effect may have been brought about by chance predominance of stimulating current in one direction or the other, according to the phase at which the stimulus began and ended.

No attempt was, however, made at the time to test this suggestion, nor was the phenomenon of differential permeability specially investigated.

The relationship of the responses (*i.e.*, changes of resistance) to the voltages of stimuli of given durations is illustrated by the curves of fig. 1. As with more massive tissues investigated previously (2 and 3), the magnitudes of the responses (shown as percentage changes of resistance) vary with the duration of stimuli of constant voltage. Thus, for example, at a voltage of 50, with

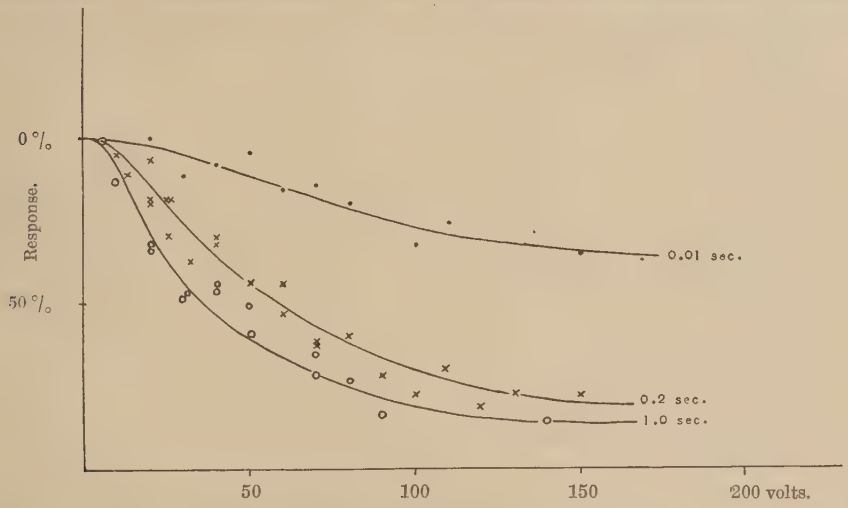

FIG. 1.—*Acacia dealbata*, stamen. 30° C. D.C.

stimuli of 0·01, 0·2, and 1·0 seconds, the responses were 12 per cent., 45 per cent., and 61 per cent. respectively.

The graph representing the relationship between the responses and the voltages of stimuli, all of the same duration, is, as in the case of Hedera and Sedum leaves, S-shaped. Furthermore, with stimuli of short duration and small voltage, positive responses (*i.e.*, increases in resistance) are indicated.

The suggestion was previously put forward (Dixon and Bennet-Clark, 3) that the S-shape of the voltage-response curve might be produced by the existence of various sizes of cells in the leaf. The chains of large cells were supposed to respond to a relatively low voltage across the leaf square, the chains of small cells requiring a high voltage; whereas the chains containing the modal number of cells respond at the modal voltage and define the point of inflexion of the curve, it was assumed that any single cell responded completely, or not at all.

Clearly, if this were true, and the tissues were uniform, the slope of the central portion of the curve would be very steep.

Support was obtained for this view by the observation that the modal voltage for a tissue is dependent on the sizes of the cells of the tissue, that is, on the modal number of cells between the electrodes. The modal voltage is linearly proportional to the modal number of cells between the electrodes.

Instead of this assumption, that a minimal voltage is required to stimulate any given cell, it would be equally valid to assume that all the cells respond to any voltage gradient across them, but to different extents, owing to the existence of individual differences of sensitivity. Since the sensitivities of the individual cells will presumably fall on a normal frequency-distribution curve, few being of high sensitivity, few of low sensitivity, and the majority of the modal sensitivity, the response-voltage curve will be S–shaped. The steep central part corresponds with the maximum on the frequency-distribution curve of sensitivities.

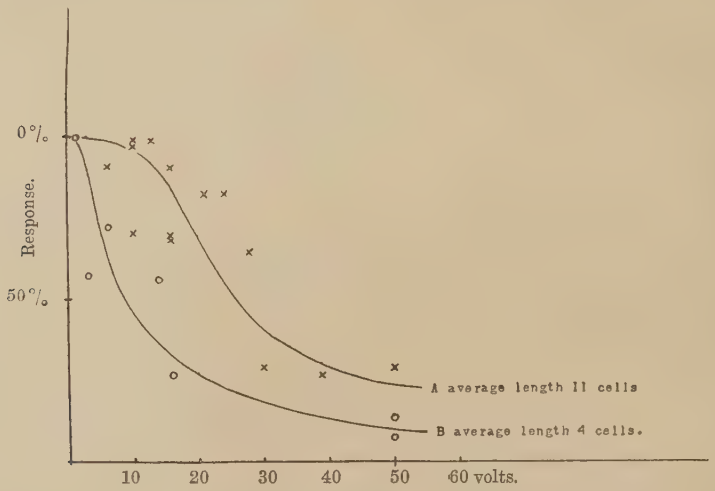

Fig. 2.—*Tradescantia zebrina,* staminal hair, 12° C. D.C.

The plausibility of such a view is evident from the facts that changes in sensitivity of tissues as a whole have been observed to take place, both when the temperature is changed, and also as the season of the year changes.

These two possible explanations have, however, been tested rather crucially by the investigation of the staminal hairs of two species of Tradescantia.

The hairs attached to the stamens of *Tradescantia zebrina* and *T. virginiana* were removed, cut across at each end, and mounted between two drops of Knop's solution, each on a platinum black electrode. These electrodes were sealed into glass tubes, which were cleaned, paraffined, and inserted into carefully paraffined corks. The conductivity of the tissue before stimulation was commonly about

10–20 times greater than that of the insulating materials, and after a stimulus it might be raised to 300 times that of the insulation.

Each staminal hair consists of a single row of cells, of which the outer walls are not easily wetted by water. The pieces employed consisted of about 8–12 cells. The sizes of the cells were variable, cells at the distal end being smaller than the others.

The relationship obtained between the voltage employed for the stimulating current and the magnitude of the response (or percentage change in resistance) is markedly similar to that found in the case of more massive tissues (fig. 2 A). The curve is a rather flat S-shape, and the point of inflection is at about 22 volts.

With a little practice it is easy to mount pieces of these hairs consisting of only 2–5 cells between the electrodes (fig. 2 B). Such pieces respond to stimuli

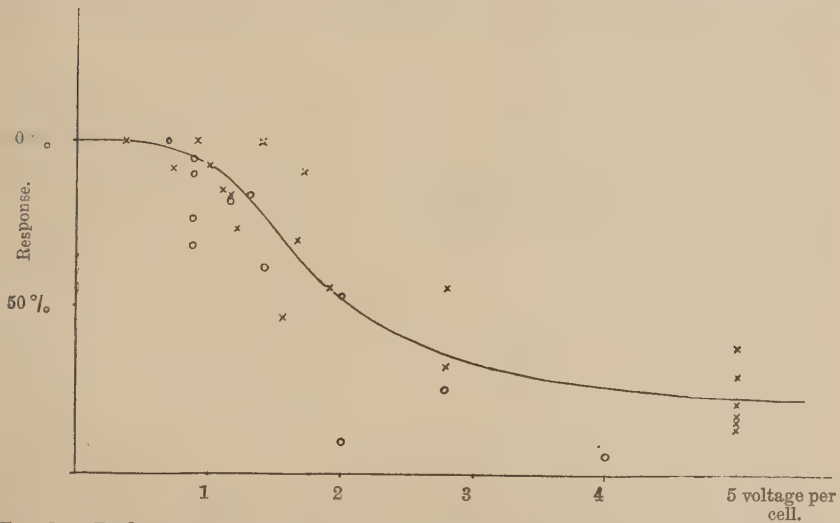

FIG. 3. — *Tradescantia zebrina*, staminal hair. D.C. Points marked X are derived from experiments carried out at 12° C. and define the curve given above. The points marked O are from experiments carried out at 31° C.

of about 1 volt, and, in consequence, it was necessary to use a considerably smaller voltage for measuring the resistance; 0·1 volt was ordinarily used for these short pieces.

Even with these short pieces the response-voltage curve is of a flat S-shape, and the point of inflection is seen to be about 5 volts.

Individual two-celled pieces recovered quite rapidly to their original resistance after having given responses as large as 30 per cent. After complete recovery from the effects of a relatively small stimulus such pieces were found to be capable of responding to suitable stimuli to extents up to 90 per cent.

It seems perfectly clear that a single cell is capable of giving responses of

different magnitudes to stimuli of different voltages. Hence the S-shaped relation is obtained with a single cell as with a massive tissue.

Our original suggestion, which would explain the shape of the voltage-response curves of a tissue, on the assumption that each cell responds either completely or not at all to a given voltage, is thus seen to be untenable. In other words, the "all or none" principle does not apply to these cells as units.

The simplest explanation of the S-shape is that it is a statistical effect, and, since it is not produced by differences between individual cells, either some smaller unit must be sought for or a completely different explanation of the shape found.

Fig. 3, in which the percentage change of resistance (response) is plotted against the voltage across each cell, indicates further the insufficiency of the "all or none" principle, with the individual cells as units, to explain our results. Evidently, if that principle held, a steep flexure of the curve at the critical voltage which completely stimulates the cell would appear.

The "all or none" explanation of the voltage-response curves might, however, still apply if a responding unit much smaller than the cell could be found in the system. Such a unit may possibly exist in the form of the droplets in the lipoid-water film bounding the protoplasts.

The experimental work which suggested the possibility of this view forms the subject of a separate investigation.

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35.

ELECTRICAL PROPERTIES OF OIL-WATER EMULSIONS WITH SPECIAL REFERENCE TO THE STRUCTURE OF THE PLASMATIC MEMBRANE.

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The work of Clowes, published in 1916 (3), has provided a simple, purely physical, explanation of the action of antagonistic ions on the permeability of living protoplasm.

The disperse phase of oil-water emulsions is water when a calcium soap is used as emulsifier, and oil if a sodium soap is used. Bancroft explained this as being due to the fact that the former soap is the more soluble in oil, and hence reduces the surface tension of the oil-surface against the soap-film to a lower value than that of the water-surface against the soap-film; the interface consequently becomes concave towards the water-phase, which, therefore, tends to become the disperse phase.*

Oil-in-water emulsions clearly are permeable to ions, whereas water-in-oil emulsions are almost impermeable. As Clowes has shown, a change from the latter condition to the former can be brought about by addition of salts of univalent metals. This phenomenon resembles the increase of permeability of living protoplasts, which is also induced by the addition of salts of univalent metals.

Clowes showed that substances such as salts of univalent cations, which caused inversion of oil-water emulsions from the impermeable to the permeable state, had a similar effect on living protoplasm, causing it to become more permeable; both permeable emulsions and protoplasm similarly became less permeable when treated with salts of multivalent cations or anæsthetics.

Now the ratio in which these opposing effects balance each other is, according to Clowes, the same approximately both in emulsions and in living tissues.

* That the surface tensions of the two phases at the inversion point are closely the same seems to be strikingly borne out by the fact that it is possible to make on a wire loop a stable film composed of a water-oil mosaic. Colouring the two phases with suitable dyes easily demonstrates that one phase is not completely enclosed by the other. Examination with reflected light supports this view.

Departure from this balancing ratio of antagonising substances produces either abnormal impermeability or abnormal permeability. In the case of living tissues this may result in the death of the protoplasts.

The hypothesis, that the limiting layer of the protoplast is a balanced oil-water emulsion of this type, offers us a surprisingly simple explanation of the otherwise almost incomprehensible phenomenon of antagonism.

In spite of its simplicity, however, this hypothesis has been criticised on several grounds.

Seifriz (18) has criticised it on two main issues: firstly, he states that in no case does sodium chloride produce inversion (increase of permeability) of oil-water emulsions, though it has this effect on living tissues. The present writers have many times tested this particular point, and have invariably found that, when the molecular concentration of sodium chloride is about 50–80 times that of the calcium chloride, inversion of the emulsion takes place, as was found by Clowes. If, however, the calcium concentration is high, as appeared to be the case in Seifriz' experiments, the quantity of sodium chloride required to obtain the necessary Na/Ca ratio may be so great as to bring about "salting out" of the soap-films. These latter stabilise the emulsion. The emulsion, therefore, separates out into its two phases when the soap-films are destroyed, a phenomenon which Seifriz records in some of his experiments.

The second objection of Seifriz is, that such salts as sodium or calcium chlorides have no effect on the phase-reversal of oil-water emulsions when substances other than soaps form the emulsifying agent.

This does not seem to us to invalidate the Clowes hypothesis in any way. There is a great mass of evidence to support the idea that there are oils in the limiting layer of the protoplast (cf., for example, Lepeschkin (10), Czapek (4), Overton (17), and others); and, further, it appears to us exceedingly unlikely that these oils should be quite pure and free from fatty acids.

If, then, the limiting layer of the protoplasts consists of a lipoid-water emulsion, in which the combined operation of a complex mixture of emulsifying agents, such as proteins, fatty acids, and other substances, determines which phase is continuous, it is evident that a change in the concentration of any one of these agents may cause phase-reversal to take place: and, although changes in the electrolyte-concentration may affect only the fatty-acid emulsifiers (as Seifriz maintains), yet an emulsion such as this will behave towards electrolytes in a manner similar to that of a pure oil-water-soap emulsion.

As recorded in a preliminary note, the present writers (7) have shown that such an emulsion resembles the cell-membrane in another important respect.

When a sufficient voltage is applied across either an emulsion or a cell-membrane (5) the electrical conductivity of each suddenly increases many times. The extent of this increase in conductivity is dependent on the potential gradient applied. Both when living tissues are used, and in the case of emulsions, it is common to find that a fifty-fold increase in conductivity takes place in the course of two seconds.

The increase in conductivity exceeds by over 1,000 times the increase which might have been expected owing to the heating effect of the stimulating current.

Both the cell-membranes and the emulsions continue to increase in conductivity after the cessation of the stimulating current, and eventually the conductivity again decreases from its maximum, and may revert to its original value.

A hypothesis of the structure of the plasmatic membrane, which explains two such apparently unconnected and remarkable phenomena as the antagonistic action of certain ions on permeability and the permeability changes produced by electric stimuli, deserves serious consideration.

In the following pages our experimental work on the effects of electric currents on the electrical conductivities of emulsions is described, and the cause of the effects is discussed.

SECTION I.

Experimental Methods.

In order to reduce the number of complicating factors as much as possible the emulsions used were prepared with few constituents. Olive oil, not specially freed from oleic acid, was used. It was emulsified in distilled water by means of sodium oleate, with additions, in certain cases, of either calcium chloride or calcium oleate.

The emulsions were not, in general, prepared by the method of Briggs (2), as, in our hands, it was found that the ingredients in the rather viscous emulsions were more adequately mixed by the process of grinding in a large mortar. As recorded by various workers, it was found to be advantageous to grind intermittently rather than continuously.

Emulsions, whether prepared by this or by Briggs' method, were found to be exceedingly variable in composition, the droplets being of very various sizes, and presumably of different compositions. The phenomenon is strikingly illustrated by the fact that stable emulsions, which lasted almost unchanged for weeks in well-stoppered bottles, were often obtained in which drops of the disperse phase contained drops of the continuous phase inside them. Only emulsions of compositions such that they were balanced between the oil-in-water and the water-in-oil state (*i.e.*, at, or close to, the inversion point) had this composite structure.

The interpretation of such microscopic observations is, however, not always easy, owing to the lens-effect of the larger drops altering the level of the focus of the droplets lying above or below. In this way a droplet lying outside a large drop may appear to be inside it.

The addition of oil- and water-soluble dyes was often found to facilitate these observations, as recorded in Section V.

The interpretation given above, however, viz., that there are droplets inside the large drops, is rendered probable by the facts that in certain emulsions in

which the water and the oil-phase were coloured blue and red respectively, the "included" drops were seen to be of the opposite phase to the larger "including" drops: a droplet in the continuous phase above a larger drop would clearly be of the same phase, and consequently of the same colour, as the larger drop.

The data of the following section also support the interpretation that droplets of one phase are actually included in drops of the other.

Conductivities were determined with a dial-bridge supplied by Messrs. Pye, of Cambridge. A small buzzer was used, and the null-point was determined by a telephone. The maximum reading possible with this bridge was 11 megohms, but the accuracy of reading such high resistances in this way was but slight.

The current coming through the buzzer appeared to have no effect whatever on the resistances of the emulsions.

Section II.

Effect of the Relative Volumes of the Phases on the Conductivity.

The object of this series of experiments was to find out the effect of alteration in the relative volumes of the phases on the state of a sodium emulsion.

Clearly, if the electrolyte concentration in the water-phase is kept constant, diminution of the ratio of volume of the water-phase to that of the oil-phase should bring about a proportional decrease in the conductivity of the emulsion.

On the other hand, if the water/oil ratio is divided by 'n,' and at the same time the conductivity of the water-phase is multiplied by 'n' by addition of more electrolyte, the conductivity of the new emulsion should be approximately the same as that of the original emulsion, unless inversion to the water-in-oil type takes place. In this case the resistance of the emulsion should become infinite. Used in this manner, the electrical conductivity is a measure of the extent to which inversion has proceeded.

In Table I, line (1), are shown the approximate concentrations of a series of sodium oleate solutions. Their specific resistances are given in line (2); and in line (3) these resistances are expressed as a percentage of the resistance of the most dilute solution.

The first five solutions were mixed with oil and converted into emulsions containing the percentages of the water-phase recorded in line (4) of the table. It will be seen readily that the extent of the dilution with oil is such that each emulsion should contain the same amount of conducting material in a given volume, and, therefore, each should have the same conductivity, if the oil behaves as an inert body.

The actual resistances found are shown in line (5). In fig. 1 they are shown as ordinates, and the percentages of water-phase in the emulsion as abscissae.

The results clearly show that when the water/oil ratio is greater than about 45/55 the resistance of the emulsions is independent of the water/oil ratio; but as the percentage of water is decreased the resistance of the emulsion more and more rapidly rises, reaching infinity asymptotically at about 3 per cent. The quantity of effective electrolyte between the electrodes probably remains constant

TABLE I.

(1).	Concentration of Na oleate.	0·2 N.	0·1 N.	0·05 N.	0·025 N.	0·0125 N.	0·00625 N.
(2).	Spec. Resist. of Sodium oleate Solutions in ohms.	160	400	780	1400	2100	3765
(3).	Resist. as per cent. of greatest.	4·3	10·5	21	37·4	56	100
(4).	Per cent. water-phase in emulsion.	4·3	10·5	21	37·4	56	100
(5).	Specific Resist. of emulsion.	1,000,000	120,000	9,100	6,630	3,760	3,760

throughout, but it may possibly be reduced in quantity to a slight extent by adsorption on the oil surfaces.

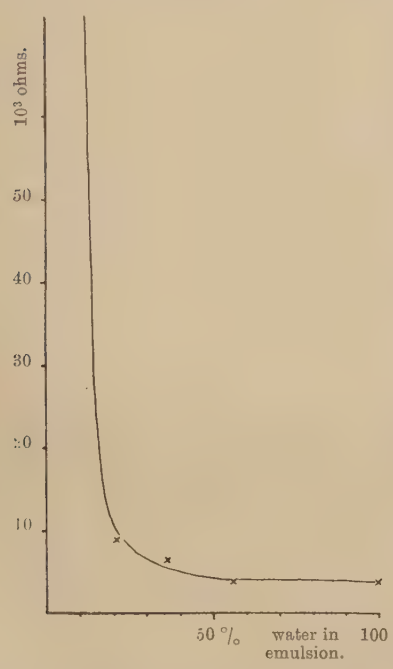

FIG. 1.—Graph showing change of resistance with change of relative volumes of phases in a sodium emulsion.

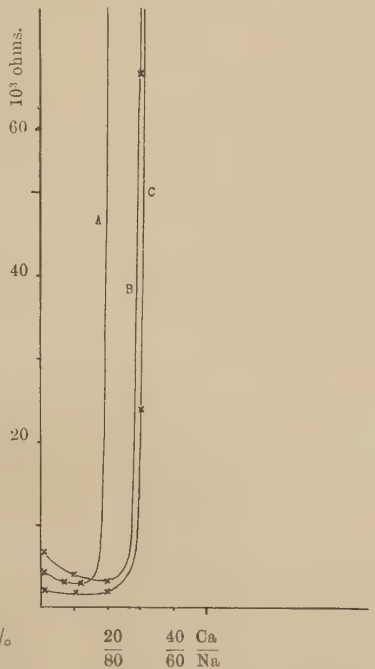

FIG. 2.—Graph showing resistances of emulsions of different calcium/sodium ratios. 10 c.c. of emulsion A contains 0·001 mol, of B, 0·0015 mol, and of C, 0·004 mol. total electrolyte.

Microscopic examination of the emulsions revealed that the real cause of the increase of resistance as the water/oil ratio decreased is that progressively more

and more of the water-phase becomes enclosed inside drops of oil, and the electrolyte thus enclosed is unable to conduct any current between the electrodes. In the end, all the electrolyte becomes enclosed in this manner and the resistance becomes "infinite," *i.e.*, almost equal to that of the oil.

The curves given in figs. 1 and 2 all indicate clearly a point which previous investigators have not emphasised, namely, that the process of change from the oil-in-water to the water-in-oil state is not a sudden one. The gradual nature of this change is due to the fact that the emulsion as a whole, when close to the inversion point, consists of a mixture of small particles of one type of emulsion dispersed through the other type. Exactly why the continuous phase becomes enclosed inside the disperse phase in gradually increasing quantities as the inversion point is approached is not easy to understand.

The gradual nature of the changes in the permeability of cells has been used as an argument against the phase-reversal theory of these changes, and indirectly against the oil-water film theory of the protoplasmic surface. The observations just recorded, bringing to light the gradual change of resistance of oil-water emulsions, show that this argument is without weight.

Section III.

Effect of the Calcium/Sodium Ratio on the Type of the Emulsion.

In these series of experiments the ratio of the volumes of the two phases was kept constant, 3 parts of water being mixed with 7 parts of oil. In addition to the oil and water, both sodium oleate and calcium chloride were present.

The results of three series of experiments are plotted as three curves in fig. 2. In this figure the resistances of a series of emulsions are plotted as ordinates, and the gram-molecular ratios of calcium chloride to sodium oleate are shown as abscissae.

The concentrations of total electrolytes differed in each of the three series of experiments: 10 c.c. of emulsion containing respectively 0·001, 0·0015, and 0·004 mol.

The results of the first of these series are shown graphically as the curve A of fig. 2. It is readily seen that as the calcium/sodium ratio is increased there is at first a decrease in the resistance of the emulsion; further increase in this ratio produces a very rapid increase in the specific resistance of the emulsion to the value of 3–4 megohms when the gram-molecular ratio of calcium/sodium is 0·43; when this ratio is 0·53 the resistance is over 10 megohms.

This very rapid rise in the resistance of the emulsion as the calcium/sodium ratio is raised from 0·33 to 0·53 is due to the inversion of the emulsion or enclosure of the electrolyte by the relatively non-conducting oil-phase.

The decrease in specific resistance as the calcium percentage is increased from zero to about 20 per cent. is presumably due to the replacement of univalent ions by bivalent. The data derived from the emulsion, in which the electrolyte was most concentrated, do not, however, show this effect.

In order to test the effect of sodium chloride on an emulsion of the water-in-oil type, an emulsion of the composition represented by the point of the uppermost curve when the calcium/sodium ratio = 0·53 was used. Its composition was as follows:—Olive oil 7·0 c.c., water 3·0 c.c., sodium oleate 0·000065 mol., calcium chloride 0·000035 mol. Each 10 c.c. contained, therefore, 0·000006 mol. calcium chloride in excess of the balancing ratio which would be obtained with an emulsion containing 0·000029 mol. To invert this mixture to the permeable form it should be necessary, according to Clowes, to add to 10 c.c. of it a quantity of sodium chloride, between 0·0006 and 0·0003 mol. The resistances of mixtures containing 10 c.c. of this stock emulsion with the quantities of sodium chloride given in the first column of Table II are given in the second column.

Table II.

Mols. sodium chloride to 10 c.c. stock emulsion.	Spec. resistance.	Ratio NaCl to excess of $CaCl_2$.
0·0003	inf.	50 : 1
0·0006	inf.	100 : 1
0·0009	2,800 ohms.	150 : 1

A quite distinct reversing action of sodium chloride is obtained, and the same effect has been frequently observed in purely qualitative experiments.

Section IV.

Effects of Alternating Currents on the Resistance of Emulsions of Different Ages.

The emulsions used in these experiments had the following composition:—Olive oil 7·0 c.c., water 3·0 c.c., sodium oleate 0·00007 mol., and calcium chloride 0·00003 mol. The specific resistances of emulsions so made up varied between 5 and 10 megohms.

For investigation they were placed in a conductivity-cell with platinum blacked electrodes, 2 mm. apart.

The effects of applying a relatively high voltage across the emulsion will be best explained by a consideration of the results of a typical experiment, such as is illustrated graphically in fig. 3. The initial resistance of this emulsion was about 5 megohms; it was placed in the conductivity-cell, as mentioned above, and an alternating voltage of 160 virtual volts (50 cycles) was applied across it for 0·5 sec.

The resistance of the emulsion was then measured at various times after this stimulus, and it was found to have decreased almost instantaneously from the original value (5 megohms) to about 200,000 ohms.

The actual resistances at various times after the stimulus are shown as the ordinates of fig. 3, and the times after the stimulus as abscissae; zero time being the moment of stimulation. For convenience of representing the data, the time scale is arbitrarily altered after the first half-hour following the stimulus.

It is strikingly shown that after the stimulus the resistance very rapidly decreases to a minimum value, which, is, however, not attained instantaneously, but usually 10–12 minutes after the stimulus. A slow, and in some cases somewhat erratic, increase in resistance follows, and in some hours the resistance of the emulsion recovers to a value somewhat similar to the original value.

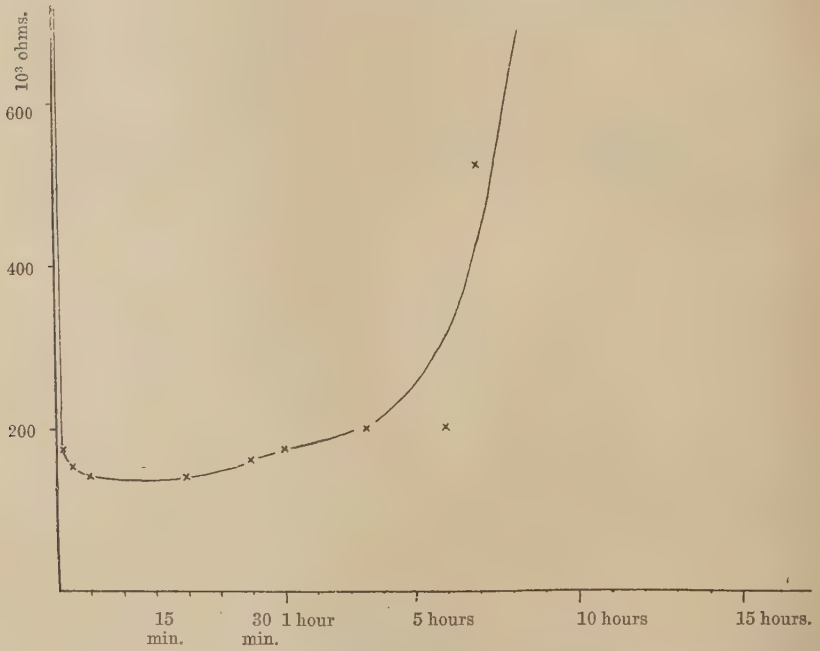

FIG. 3.—Graph showing the change in resistance of an emulsion after stimulation by an A.C. of 160 volts for 0·5 sec. given at zero hour. Note the change of the time scale after the 30th min. Original resistance approximately 5 megohms.

Clearly, the electric stimulus has caused the emulsion, which originally was almost impermeable to ions and water-soluble substances, to become fairly permeable. The results may be profitably compared with the effect produced on a living tissue by the application of an electric stimulus to it.

In a general way it is known that electrical stimulation will cause the permeability of any living tissue to increase (M'Clendon, 13), but only few tissues form really suitable subjects for quantitative examination. Many workers have, moreover, failed to observe any increase of permeability owing to their use of too low a voltage of stimulating current, which should be of the order of 1–2 volts across each cell.

With a suitably large stimulus one finds that the conductivity (permeability to ions) suddenly increases at the moment of stimulation, and the increase is continued for some minutes after the cessation of the stimulating current. The conductivity then slowly recovers from its maximum value. (See, for example, Dixon and Bennet-Clark, 5, fig. 3.)

The similarity of behaviour of the emulsion and the living tissue is very striking.

A series of experiments were designed to test the constancy of behaviour of this particular emulsion stock.

After recovery from the first stimulus of 160 volts A.C. for 0·5 sec., the same stimulus was applied a second time. The minimum resistance after the stimulus was this time 145,000 ohms, whereas before it was 140,000 ohms. Other samples of emulsion from the same stock were removed at different times for stimulation by stimuli of the same magnitude.

The minimum resistances after these stimuli and the time in hours, at which the stimulus was applied after the making of the stock emulsion, are noted in the table below:—

Table III.

Age of emulsion in hours.	Spec. res. after stimulus.	Age of emulsion in hours.	Spec. res. after stimulus.
0·5	145,000	18·00	110,000
17·0	120,000	18·25	100,000
17·5	150,000	25·00	58,000
17·75	140,000		

The results show that the sensitivity of the emulsion may alter quite rapidly. Actually, this sample of emulsion became inverted to the permeable oil-in-water form 96 hours after it was prepared.

One of the simplest explanations of this ageing effect is that solution of atmospheric carbon dioxide removes calcium ions from solution in the form of calcium carbonate. As will be shown later, the removal of calcium ions brings about an increase in the sensitivity of emulsions to electrical stimulation.

Some support for this explanation is obtained from the following experiments:—

Two stock emulsions were prepared of the following compositions: (*a*) Olive oil 67 c.c., water 33 c.c., sodium oleate 0·0027 mol.; and (*b*) olive oil 67 c.c., water 33 c.c., and calcium oleate 0·07 mol. These two stock emulsions were mixed in various proportions, and it was found that if the percentage of stock 'b' was more than 20 the resulting mixed emulsion was of the water-in-oil type, but otherwise it was of the oil-in-water type. At the inversion point the molecular ratio of calcium to sodium is in this case 6 : 1.

This ratio is considerably greater than is usually needed; the reason for this may possibly be that much of the calcium oleate is not in solution. In other words, stock 'b' is saturated with calcium oleate. Microscopic examination revealed solid particles in this emulsion, which were presumably undissolved calcium oleate.

The emulsion containing 28 per cent. of stock 'b' and 72 per cent. of stock 'a' responded readily to stimuli of 200 volts for 0·5 sec., but it was noted that as the stock of mixed emulsion got older it became less sensitive, in contradistinction to the other sample of emulsion mentioned above, which became more sensitive.

The age in hours and the final resistance in ohms after a stimulus of 200 volts for 0·5 sec. are shown for this emulsion in Table IV.

TABLE IV.

Age of emulsion.	Final resist. after stimulus.
0·5	157,000
17·0	755,000
24·0	1,800,000
48·0	No change

The explanation of this alteration which suggests itself is that the freshly-prepared emulsion is not in equilibrium with the undissolved calcium oleate, and that the process of saturating the oil and water phases of the added stock 'a' is a relatively slow one. If a gradual increase in the calcium concentration of the emulsion, such as this, were to take place the sensitivity would decrease in the manner actually observed.

Owing to the large excess of undissolved calcium oleate it is to be expected that atmospheric carbon dioxide will have no effect on the calcium concentration.

SECTION V.

Effect of Calcium: Sodium Ratio on the Sensitivity of Emulsions.

Of all the factors which affect the magnitude of the change in resistance of an emulsion when a given voltage gradient is applied across it, the one which appears to exercise the most marked effect is the ratio of calcium to sodium in the emulsion.

That ratio, at which the surface tensions of each phase against the interfacial soap-film are equal, may be conveniently called the inversion ratio.

When more sodium is present the emulsion is in the oil-in-water state, and conversely, if the calcium is in excess, the emulsion is in the impermeable water-in-oil state. Actually, the transition is not absolutely sharp owing to the unevenness in composition of emulsions prepared by the ordinary methods.

When the composition is close to the inversion ratio, but with a slight excess of calcium, the emulsion is found to consist of a mixture of irregularly-shaped drops of oil-in-water emulsion distributed through a water-in-oil emulsion, and the greater the excess of calcium the smaller is the quantity of oil-in-water emulsion, and consequently the higher the resistance.

The expectations are realised that the greater the calcium/sodium ratio the less readily is the emulsion converted from the impermeable state to the permeable.

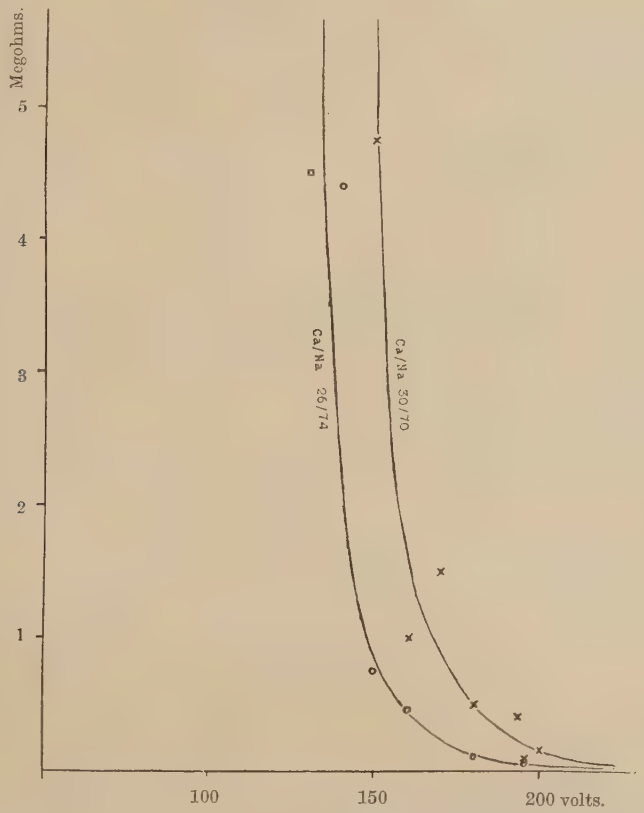

FIG. 4.—Graph showing the relation between response and voltage of A.C. stimuli applied for 1 sec. to two emulsions of different calcium/sodium ratios. The resistances of the emulsions before stimulation were over 10 megohms. The ordinates show the minimum resistances attained after stimulation.

This is shown, for example, by the curves of fig. 4, obtained as follows:—Emulsions were used of the following: calcium/sodium ratios, 30/70 and 26/74; the total electrolyte concentration was 0·0001 mol. per 10 c.c. of emulsion, and the percentage of water-phase to total volume of emulsion was 30 per cent. in all the emulsions. The emulsions were placed in the conductivity-cell, as before, and various voltages, as shown by the abscissae, were applied across the emulsions for 1 second.

The final resistance after the stimulus is shown by the ordinates. The initial resistance before stimulation was in all cases over 10 megohms.

The two curves show the relationship between the voltage of the stimulus and the magnitude of the responses evoked in emulsions of which the calcium/sodium ratio is recorded on each curve.

It is seen that with a given voltage of stimulus the magnitude of the response is smaller, the larger the percentage of calcium in the emulsion; and, correspondingly, the minimum voltage at which a response of measurable magnitude is evoked is higher, the larger the percentage of calcium.

The significance of the shapes of these curves can be made plain by a consideration of the one relating to emulsions, of which the calcium/sodium ratio is 30/70.

Whilst a voltage of 145 does not reduce the original resistance of this emulsion to a value of less than 10 megohms, a voltage of 150 reduces it to a value of 4·75 megohms, and 160 volts causes the resistance to fall to about 1·5 megohms.

Further increases in voltage of the stimulus produce successively smaller increases in the magnitude of the response evoked.

Unfortunately, we possess as yet no data of the change in resistance brought about by lower voltages than 145, nor was the initial resistance of the emulsion known. The mechanism of the effect is made easier to understand when one supposes that this unexplored upper part of the curve forms a continuation of the lower part as a regular S-shaped curve.

The gradually increasing increments of response for a given increase of voltage would then be due to the gradually increasing numbers of droplets of water-phase of sufficiently low calcium/sodium ratio to be affected by the voltage.

When the applied voltage is just high enough to affect the droplets of modal calcium/sodium ratio, half of them should respond.

Finally, for further given increases of voltage, successively fewer additional droplets of greater and greater calcium/sodium ratios will respond; and, consequently, the increments of response become smaller for equal increments of stimulus.

The S-shaped response-voltage curve may be derived in this way from the (presumed) normal frequency-distribution curve of calcium/sodium ratios of the droplets of water-phase.

A stimulus of sufficient magnitude to reduce the surface-tension of those water-drops, of which the surface-tension is equal to, or less than, the modal surface-tension to the same value as that of the oil-surface, may be described as a "modal stimulus."

Such a stimulus should affect half of the drops, and should leave all the droplets of which the surface-tension is larger than the mode unaffected in shape.

Each successive equal increment in the stimulus would bring about successively smaller increments in the number of additional droplets affected, and consequently the "response-stimulus" curve should be S-shaped.

Section VI.

The Appearance of an Emulsion whilst Changing in Resistance under the Influence of an Electric Current.

In the explanation suggested above of the shape of the response-voltage curves, and also in previous sections, we have assumed, as the experiments of this section show, that the decrease in resistance of an emulsion following an electric stimulus is due to the partial phase-reversal or inversion of the emulsion.

For these experiments, in order to distinguish the phases readily, colouring matters having different solubilities in the two phases were added to the sensitive (nearly balanced) emulsions. Phenol-phthalein, which colours the water-phase red, Sudan III, which colours the oil-phase red, and bromthymol blue, which colours the water-phase blue, were found suitable for this purpose. Many blue and green dyes do not tint the water-phase deeply enough owing to their insufficient solubility; and other stains, being supplied as oxalates of the bases, form precipitates with the calcium salts of the emulsions, and are consequently unsuitable.

The emulsion, coloured by one of these methods, was spread as a thin film between platinum electrodes fixed about 3 mm. apart on a microscope-slide placed under a microscope, and the emulsion was watched as the stimulating current (200 volts, A.C.) was applied.

At the moment of application of the stimulus to a sensitive film, a series of "flicks" or explosions appear to take place in various parts of the film. On close examination it is seen that these are due to the sudden coalescence of previously separate water-drops or particles of oil-in-water emulsion to form larger masses of water, almost invariably with oil-drops enclosed inside them, and frequently of an elongated shape. These often spread out upon the glass-surface in contact with the emulsion, and so become much less visible.

In many cases it was observed that the spherical water-drops distributed through the oil suddenly lost their spherical shape on application of the stimulating current.

In one case, this loss of spherical shape of the water-drops was followed immediately by the separation of the interstitial oil into nearly spherical masses, with the water forming the continuous phase.

The effective stimuli appear to act by causing the interfaces originally concave towards the water-phase to become concave towards the oil-phase. So that either partial or, in extreme cases, nearly complete inversion takes place.

Section VII.

Effect of Voltage and Duration of Direct Currents on the Response.

The experimental results to be described in this section, though they lead us to certain interesting quantitative conclusions, are, unfortunately, not entirely free from slight uncertainties owing to the rather rapid changes in the sensitivity of emulsions which we have already described.

An emulsion made up of 3 parts of water and 7 parts of oil containing 0·00007 mol. sodium oleate and 0·00003 mol. calcium chloride in 10 c.c. of the

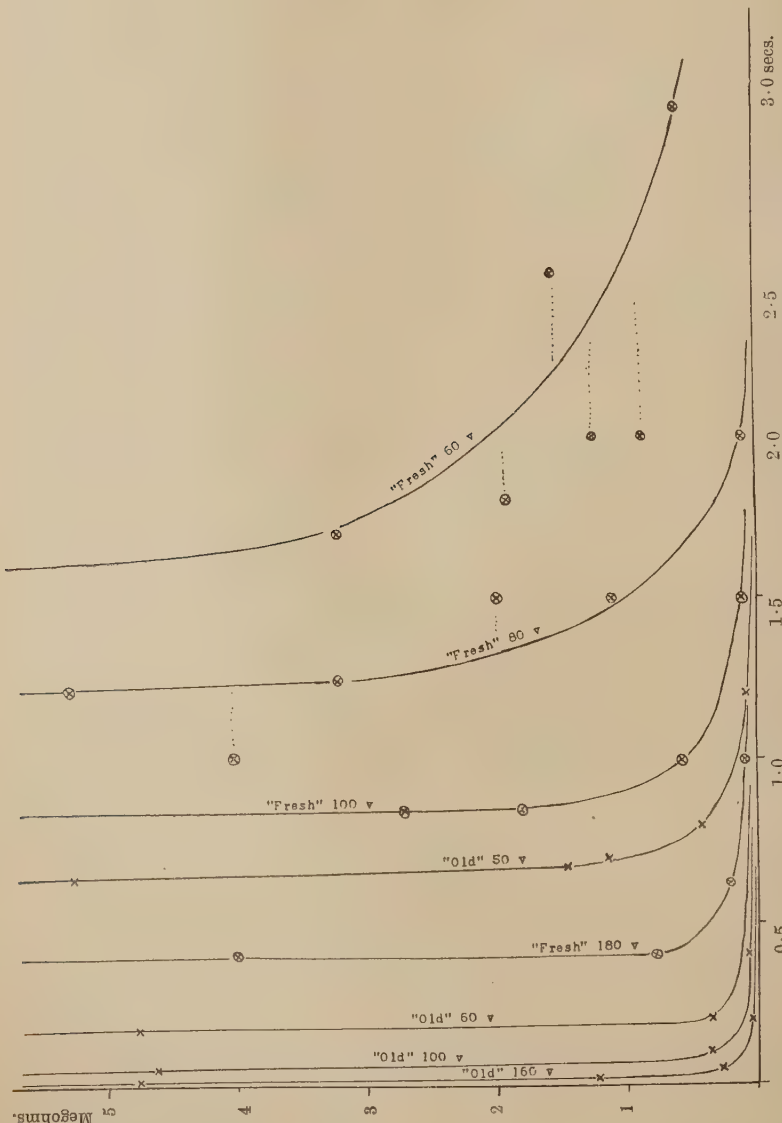

Fig. 5.—Graph showing the relationship between the responses (final resistances) and the durations of D.C. stimuli given to "old" and "fresh" emulsions. The voltages of the stimuli and the ages of the emulsions are noted on the curves. Before stimulation the resistances of the emulsions were over 10 megohms.

emulsion was used in all these experiments. To it stimuli of different voltages and durations were applied.

The magnitudes of the final resistances are shown graphically as ordinates in fig. 5, the abscissae being durations of the stimuli which evoked these responses. A number of different voltages (D.C.) were used; and each curve corresponds to a series of stimuli of a given voltage. The voltage used in obtaining each curve is noted in the graph.

Two groups of curves are plotted in the figure; one was obtained while the emulsion was between 0·5 hour and 1·5 hour old, and the other group was obtained 24 hours later. The shift of the curves towards the left on the second day illustrates the enormous increase in sensitivity which has taken place.

The curves of each group are distinguished by the notes "Fresh" and "Old" before the note of the voltage on the graph. The former refers to the fresh, and consequently relatively insensitive, emulsion, and the latter to the 25-hour old emulsion. Circles and crosses also distinguish the former group of observations from the latter, which are represented by crosses (x).

Examination of the figure shows that, though the observations are few, they can, in all but two cases, be fitted fairly readily to regular curves. The points on the two curves for which the time factor is longest show greater irregularities.

The chief interest in the two groups of curves is that one can obtain from each the values of the liminal duration of stimuli of certain voltages to evoke a response. Further, the effect of age is shown to be a very marked one.

It will be noticed that strikingly small stimuli affect the emulsion in its sensitive condition. For example: 30 volts D.C. for 0·7 sec. caused the resistance of a layer 2 mm. thick to change from the initial value of over 10 megohms to about 1 megohm, and when this stimulus was continued for 1 sec., instead of for 0·7 sec., the resistance fell to about 130,000 ohms.

DISCUSSION.

In order to obtain an idea of the various factors which may operate to cause inversion of a water-in-oil emulsion when an electric stimulus is applied to it, it is convenient to consider first the effects of passing a current through a somewhat simpler system.

Each water-drop in one of these emulsions and the mass of oil surrounding it may be regarded as an oil-chain of the following parts:—oil; soap-film; water; soap-film; oil.

Moreover, it must be expected that the molecules of soap in the oil-water interface are orientated with their polar carboxyl-groups directed towards the water-phase. Recent work by McBain suggests further that, in addition to the monomolecular surface-layer, supernumerary molecules are attached to this layer in the manner of filings attached to a magnet.

In the case of an oil-soluble calcium-soap, these extra molecules may be expected to be attached on the oil-side of the surface-layer; water-soluble soap molecules being attached on the water-side.

Several changes will take place when a current is passed across such a system.

If only one electrolyte is distributed in equilibrium between the several phases, the passage of the current will cause it to decrease in concentration at one oil-water boundary, a corresponding increase in concentration taking place at the other boundary.

The direction of movement of electrolyte relative to the direction of the current and the magnitude of the change of concentration produced by a given quantity of current have been shown by Nernst and Riesenfeld (16) to depend on the relative magnitudes of the transference-numbers of the ions in the two phases.

Nernst's theoretical treatment appears to be incorrectly quoted by Michaelis (14).

In the case we are considering, where both sodium oleate and calcium oleate are present, it is not possible with the data at our disposal to predict whether both electrolytes will accumulate at the same interface or not; it is, however, almost certain that the ratios of calcium to sodium at the interfaces will not remain the same as before the passage of the current.

This factor operating alone may be expected then to cause the interface at one side to become more convex towards the oil-phase, and the interface at the other side to become more concave towards the oil-phase in terms of Bancroft's hypothesis.

Other important changes take place which may be of greater significance for an understanding of the inversion of emulsions since the quantities of current used as stimuli are invariably small.

The passage of a current across the system will cause the polar ends of the oriented molecules of the surface-layer to direct themselves towards the anode instead of towards the water-phase, so that at the anode side of the system there will be a considerable stirring up of the surface-layers. Some stirring of the supernumerary layers may also be expected at both anode and cathode sides of the system.

It is well known that the static surface tensions of soap-solutions are commonly as low as a third of that of pure water, whereas the dynamic surface tensions are usually of the order of three-quarters that of water.

Hence this stirring up of the interfacial soap-layer by the current will most probably affect the phase-relations of an emulsion to a considerable extent.

It appears to us impossible to predict at present whether this stirring would affect only one side of each drop (the anode side), or whether both sides would be affected. It seems equally difficult to predict whether the interface will become concave towards the oil or not as a result of the operation of this factor.

Besides the possible operation of these factors on the surface tensions of the two phases against the interfacial soap-film, the possibility must be borne in mind that the charges on the two phases relative to the soap-film may be altered by the application of the stimulus. Since the interfacial tension would be decreased

by an increase in the charge, it is possible that the surface tension of the water-phase against the soap might be more decreased than the surface tension of the oil-phase against the soap, and thus inversion of the emulsion would take place.*

These explanations possess the common feature that the effectiveness of the stimulus depends on the quantity of electrolyte moved by the stimulus and on the rate of diffusion. A test of the hypothesis advanced may be obtained from the following considerations.

The quantity of electrolyte which accumulates in the boundary layers of the water-droplets depends on two factors: the greater the quantity of current passed the greater will be the quantity of electrolyte accumulated; but when a given quantity of current is applied in a very short time (*i.e.*, at a high pressure), the quantity accumulated at the end of the period of application of the current is larger than when the same quantity is applied during a longer time (*i.e.*, at a lower pressure).

The reason for this is that backward diffusion of the electrolyte from the concentrated boundary-layer into the more dilute central part of the drop is more effective in reducing the concentration of the boundary-layer the longer the time for which it is allowed to act.

Nernst (15) worked out the relationship between the voltages of the current and the times for which they had to be applied to bring about a given alteration of concentration of electrolyte at the boundary-layer.

He showed that where a number of stimuli of different voltages and durations are applied, if the voltage $\times \sqrt{\text{duration}}$ is kept constant, the increases in concentration at the boundary-surfaces in the system are equal. This principle does not apply to very long durations.

It consequently follows, from the hypothesis advanced above, that the voltage $\times \sqrt{\text{duration}}$ of modal stimuli to a given emulsion should be constant over a considerable range of voltages.

The experiments recorded in Section IV test this particular point.

Two groups of experiments were made; one, when the emulsion was freshly prepared and relatively insensitive, and the second 24 hours later. The curves plotted in fig. 5 show the results of both groups of experiments.

The points of each curve indicate the relationship between the final resistance of the emulsion and the duration of the stimulus applied to it.

Each curve refers to stimuli of a definite voltage, which is written beside the curve. Those curves marked "Old" were obtained from the emulsion when it was in a sensitive state, whilst those marked "Fresh" were obtained from the freshly-prepared emulsion.

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* Dr. H. H. Poole, has pointed out to us that the stimulating current might also have the purely electrostatic effect of causing the water-drops distributed through the oil to elongate in the direction of the electric field, and as they would thus come closer to each other, the electrical forces tending to draw them out would become greater, so that ultimately they might coalesce into continuous tubes joining the electrodes.

In Table V, below, in the first column, are given the voltages used with the sensitive and with the insensitive emulsion. The durations, for which each voltage had to be applied to cause the resistance of the emulsion to fall from its original value to the modal value of about 4 megohms, are given in the second column. In the third column are given the corresponding values of the expression voltage $\times \sqrt{\text{duration}}$.

TABLE V.

Voltage applied. Sensitive group.	Duration in seconds.	Voltage $\times \sqrt{\text{duration}}$
30	0·65	24·2
60	0·18	25·6
100	0·05	22·4
160	0·015	19·6
Insensitive group.		
60	1·65	77
80	1·24	89
100	0·85	92
180	0·40	114

When the possibility of variation in composition and sensitivity of the emulsion samples is considered, it must be admitted that more constant values for the figures in the last column could hardly have been expected on the basis of the hypothesis advanced.

In conclusion, we see that the assumption that the limiting plasmatic membrane is formed of an oil-water emulsion explains the following observations:—

Permeability is increased by univalent cations, as, for example, by sodium salts.

This effect is prevented, or with sufficient concentrations reversed, by the addition of salts of bivalent metals; the phenomenon being known as "antagonism."

Permeability is decreased by various narcotics, alcohols, &c.

The passage of an electric current above a certain limiting magnitude through a tissue causes the permeability suddenly to increase enormously, and a further slight increase takes place for some minutes after the stimulating current has ceased; finally, the permeability decreases, and, unless the tissue has been injured, recovers again to its original impermeable state.

The magnitude of this change in permeability is related to the magnitude of the stimulus which evoked it by an S-shaped curve.

Changes in permeability are generally not sudden.

It is possible that the hypothesis might be extended to give a definite meaning to the deductions of Nernst and Hill for the conditions necessary to bring about

excitation of nerve and muscle if it is assumed, as has been suggested (Lillie, 11; M'Clendon, 13), that excitation is the accompaniment of a change in permeability.

The relations between liminal voltage of stimulus and the duration, when direct currents are used, and the liminal voltage and the frequency in the case of alternating current stimuli suggested the theory that excitation is induced by a certain increase in concentration of ions at semi-permeable membranes in the excitable tissue (Keith Lucas, 12; Hill, 9).

The quantitative results obtained experimentally agree closely with those predicted from the theory.

As pointed out previously, a certain increase in concentration of electrolyte at the surfaces of the water-drops in a water-in-oil emulsion brings about "excitation" or increase in permeability of the emulsion. The same relation between voltage, frequency and duration ought also to apply in this case.

This has been found experimentally in the case of the relation between voltage and duration of the liminal direct current.

It may also be pointed out that the observed effects of the influence of calcium salts on the sensitivity of nerve and muscle would receive a simple explanation in terms of this hypothesis of the nature of the plasmatic membrane of the cell.

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No. 36.

STUDIES IN PEAT—PART 4: LOW TEMPERATURE CARBONISATION UNDER VARIOUS CONDITIONS.

By COLM O'SULLIVAN, A.R.C.Sc.I.,

AND

JOSEPH REILLY, M.A., D. ès Sc.

[Read January 28. Published separately April 8, 1930.]

In previous experiments (Sc. Proc. Roy. Dub. Soc., **19**, No. 29, 1929), samples of air-dried peat in quantities of 500 grams were subjected to mild carbonisation at 550° C. in an electrically heated retort, and the resulting tars were examined by a mode of selective solvent extraction. The most notable result of this work was the large quantities of tars produced, and it was accordingly decided to examine further into the nature of the decomposition of peat and various constituents of peat (*e.g.*, crude peat wax and the humic and cellulosic portions) under conditions of mild carbonisation. Consideration was given in the first instance to the effect of acids naturally present during the process of decomposition; their influence was counteracted by carrying out a distillation in an alkali medium. Attention was then directed to the wax constituent, and separate distillations were performed on the wax and non-wax portions of the peat. It is intended to extend the work later to the humic and cellulosic fractions.

Distillation in Alkali Medium.

450 g. of powdered black peat were intimately mixed with 50 g. of dried calcium carbonate and carbonised under the same conditions, and the resulting tars collected and examined in the same way as in previous distillations of peat. The time required for complete carbonisation and the yields of tar, wax, and resin proved to be in very close agreement with those previously found for straight distillations of the peat alone. The subjoined table (I) shows the comparative figures for the yields obtained, expressed as percentages of the weight of anhydrous peat distilled.

Table I.

	Tar soluble in ether.	Resin soluble in alcohol.	Wax soluble in acetone.	Light Oil.
Peat	14·58	0·21	0·41	1·42
Peat + 11% Calcium carbonate	14·36	0·32	0·40	1·39

These results would appear to indicate that the presence of either weak acidic or alkaline substances during the carbonising process has no appreciable effect on the rate of decomposition of the peat, or on the quantities of tars evolved.

Wax in Peat.

Inquiry was next directed to the influence of the comparatively large proportion of acetone-soluble material contained in the peat. This crude wax, forming, as it does, about 10 per cent. of the dried peat under observation, would, it was thought, be responsible for a considerable share of the tars evolved. The smallness of the quantity of wax which appears in the products of distillation confirms this view. Besides, it appeared to be of interest to ascertain what contribution the wax made to the resulting tars, and what part it played in the process of carbonisation. It was, accordingly, decided to extract the wax from the peat, and subject both wax and residual peat to separate distillations under the same conditions as before.

Wax, like most other constituents of peat, varies appreciably in content with the locality and age of the bog and the plants from which the peat is derived. Wiegmann, in his proximate analysis of the constituents of peat, reports as much as 6·2 per cent. wax in a high-bog peat containing 5·3 per cent. moisture, and as little as 0·25 per cent. in a dredged variety containing 12·2 per cent. moisture—the samples being, apparently, artificially dried. The peat under examination by the authors has been found, on extraction with acetone, to yield upwards of 10 per cent. crude wax, calculated on the dry sample. This material was not further purified, but used in this condition for the subsequent experiments.

Extraction of Wax from Peat.

In order to provide sufficient wax for a large-scale distillation under the same conditions as obtained in previous distillations of the peat, it was decided to extract a kilogram of peat. Repeated treatment of the peat with small quantities of acetone and, in each instance, warming to assist solution, decanting the extract, and finally distilling each extract, would prove too slow and laborious, and, in view of the many operations involved, wasteful of solvent.

A method of continuous extraction on the Sohxlet principle was accordingly devised (fig. 1). The flask to contain the peat was fitted with two reflux condensers in series, and reaching to the bottom was a siphon tube, the mouth of which, consisting of a thistle funnel, was loosely packed with peat fibre to serve as a filter for the peat dust when siphoning took place. The fibrous portions being selected to form the bottom layer, the peat was introduced into the flask, which was then half-filled with warm acetone, and placed in a water-bath. The flask was then connected, as shown, with the vaporiser, which consisted of another flask containing the solvent, heated in a bath of calcium

chloride solution. The acetone was vaporised so as to condense and fall in a steady trickle on the peat. The addition of a second condenser served to hasten the process of extraction which proceeded continuously, siphoning taking place at regular intervals of about 25 minutes. After 15 hours' continuous extraction, the acetone extract which siphoned over was almost colourless, and the process was stopped. The vaporiser, which now contained the extracted matter, was disconnected, and the acetone completely distilled, leaving the crude dry wax, which was weighed and then removed from the flask for subsequent distillation.

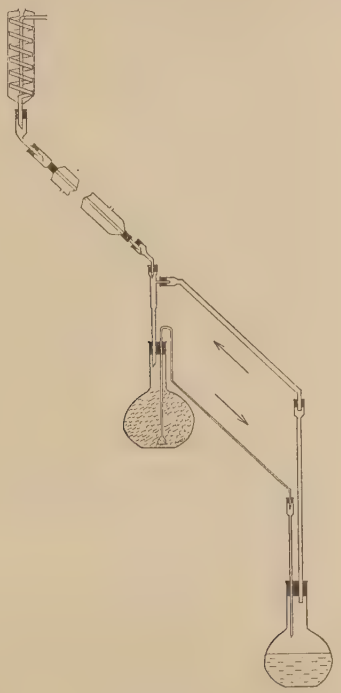

Fig. 1.

Distillation of the Wax-freed Peat.

The residual wax-freed peat (*i.e.*, acetone-insoluble portion) was shaken out of the other flask and spread out to dry. 500 g. of the dry material were then charged into the carbonising retort, and subjected to the usual distillation, the tars being collected and extracted as before. This carbonisation disclosed no new features, the usual immediate products of the decomposition of peat being represented in the distillates. Interest is centred mainly in the percentage yields of the various products which are shown in Table II, and are discussed below in conjunction with the corresponding quantities in respect of the wax.

Distillation of the Wax.

The wax could not be charged into the retort in the same manner as the peat, lest, on melting, some of it should flow out unchanged into the first receiver. A boat to fit into the inner container of the retort and retain the wax seemed the most desirable container to employ for the purpose. This was provided through the kindness of Messrs. Henry Ford & Son, Ltd., who constructed for the authors a boat of sheet steel of the required dimensions. The arrangement is shown in section in fig. 2. The boat rests inside the inner cylinder of the retort, and is held in position between two perforated iron discs fixed one at each end of the cylinder, through the centre of which projects an iron tube for holding a thermo-couple. The inner container is secured by means of a

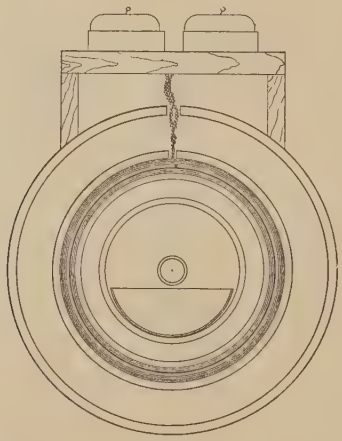

Fig. 2.

horizontal flange to an outer closed cylindrical jacket, leaving an annular space of about half an inch between the two. The outer jacket is heated by means of two electrical windings giving temperatures up to 250° and 650° respectively. This jacket is packed and permanently fixed into an iron casing.

A preliminary distillation, using about 10 g. of the wax, was carried out to ascertain the nature of the decomposition, and this indicated products similar to those obtained from peat. It was therefore decided to use the same receiving apparatus as was used for the peat. 50 g. of the wax were weighed into the boat, warmed to incipient melting, and allowed to cool, when the wax formed a layer adhering firmly along the bottom of the boat, thus enabling the wax to be charged into the retort, which requires to be bolted and screwed in the vertical position. The distillation was performed as usual, and the products, which took almost 4½ hours for complete evolution, were collected and examined.

Table II.

Percentage Yields calculated on dry samples.

	Total Heavy Tar.	Tar soluble in ether.	Resin soluble in alcohol.	Wax soluble in acetone.	Light Oil.
Peat	15·53	14·58	0·21	0·41	1·42
Wax-freed Peat ...	9·64	8·5	0·24	0·59	1·16
Wax	70·25	67·24	0·83	0·52	—

The results of the separate distillations of the wax and non-wax portions of the peat and the corresponding quantities previously obtained by direct carbonisation of peat are shown in Table II (above). The most striking features of these results are the high percentage yield of tar and the absence of light oil in the case of the wax, and, as regards the wax-freed peat, the low yield of tar and the comparatively large quantity of light oil. Of principal interest, however, is the large proportion of tar contributed by the wax, which is better shown by the following Table III:—

Table III.

Comparison of Yields by Direct and Indirect Carbonisation.

	Total Heavy Tar.	Tar soluble in ether.	Resin soluble in alcohol.	Wax soluble in acetone.	Light Oil.
89·7 g. Wax	63·01	60·33	0·74	0·47	—
910·3 g. Wax-freed Peat	87·78	77·36	2·19	5·37	10·56
Totals.					
1000 g. Peat (Indirect Carbonisation)	150·79	137·69	2·93	5·84	10·56
1000 g. Peat (Direct Carbonisation) ...	138·2	129·82	1·86	3·64	12·66

Thus it appears that more than 40 per cent. of the tar produced by indirect carbonisation is derived from the wax constituent, which is present to the extent of about 10 per cent. in the peat in question. Whether this holds true to quite

the same extent in the case of direct carbonisation of peat alone is not certain, but it is evident that the yield of tar from peat depends largely upon the proportion of wax contained in the peat. The increased quantity of tar obtained by the indirect method seems to be due to the fact that, with separate distillation of the wax, the products of the decomposition are swept away from the source of heat more rapidly and completely than in the case of carbonisation of peat, where some of the tar vapours, particularly those evolved at lower temperatures, are held in the retort by the surrounding peat particles, and partially condense, being later, at higher temperatures, subject to cracking and consequent gasification.

It will be of further interest to examine and compare the acidic, basic, and other constituents of the various tars obtained in these experiments after a detailed investigation has been made along the lines of the previous work in peat. This investigation is now in progress, and will form the subject of a further communication.

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No. 37.

THE APPLICATION OF GAMMA RADIATION TO DEEP-SEATED TUMOURS.

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[Read April 2. Published separately April 16, 1930.]

The fact that gamma radiation cannot be brought to a focus by refraction or reflection militates against its usage in certain cases. I refer to difficulties which must arise when it is sought to radiate tumours so placed as to render needle-treatment impossible, while, at the same time, so deep-seated as to call for rays of considerable intensity in order to reach them from without.

In such cases it should be possible to produce the effects of a focal concentration of the rays by the obvious plan of causing two independent beams to intersect one another at the site of the tumour. Or, again, we may cause one only beam to describe a conical track, the apex of the cone being within the tumour. These methods, as applied to X-rays, have been studied many years ago, and are described in an article in Vol. 20, No. 6, of the Archives of Radiology, November, 1915, by Robert Knox, M.D., and A. St. George Caulfield.

It appears, however, that the results obtained by this early work with X-rays were disappointing. Many reasons might be given for this. The unwieldy nature of the required installation creates serious difficulties, and is inimical to reliable quantitative work. The compact and convenient form which might be given to the apparatus when gamma rays are being dealt with, as well as the well-known superiority of gamma radiation as contrasted with X-rays in dealing with malignant growths, suggests that the failure of such methods with X-rays must not be supposed to involve similar failure in the case of gamma rays.

I shall now describe an applicator which I designed some time ago when in ignorance of the earlier work with X-rays.[1]

Referring to the figure, we see in vertical section a cylindrical box, drawn to ¾ of full size. It is, preferably, made of aluminium. It is supposed to be resting on the patient and located above a malignant growth; as defined by previous exploratory work with X-rays.

[1] I have to thank Dr. Woodburn Morrison, writing from the Royal Infirmary, Edinburgh, for directing my attention to the early work with X-rays. See also letters in the *British Medical Journal* of March 8 and 15, and *The Lancet* of March 8, 1930.

Two radiators, of platinum, gold, or lead, are shown in use. They are lettered *R*. Each carries a charge of radium located in the upper closed end. As inclined in the figure the rays from these radiators cross at the level of the tumour. The radiators may be inclined at any desired angle with the vertical.

These radiators are attached to the roller lettered *Rl*. When this roller rotates the inclined beams describe a conical path. In the figure the apex of the cone is near or within the margin of the tumour.

In order that the gamma rays may travel around the tumour, the plan of the tumour, as revealed by radiograph, is copied on a template of thin wood. This template is shown in section and marked *Tp*. The roller *Rl* is kept in contact with the edge of the template by the pull of the spiral spring *S*, in a manner which will be understood from the figure.

The rod within the spiral spring *S* passes freely through the lower end of a vertical spindle, marked *D*. To *D* the drive, or source of rotation, is attached (not shown). Preferably this is a simple piece of clockwork, which when wound up will run steadily and at an adjustable rate for some hours. It may, of course, be pneumatic or electrical, etc.

The action is now obvious. The rotation of *D* carries with it the roller *Rl*; this being supported by the rod around which the tension-spring *S* is coiled. The roller, following the curvature of the template, carries the rotating beam of gamma rays from the radiators along the margin of the tumour, or within it, according to the form and dimensions of the template. A single radiator may, of course, be used if desired.

The entire apparatus is designed so as to be simple in construction, easily opened and closed. It is preferably constructed of aluminium or other light material. The apparatus is intended to be attached to the patient by bandages, so that it may be worn without discomfort. It is evident that this system of irradiation, applied to the tumour, is entirely in the hands of the surgeon; being controlled by the form given to the template; the inclination of the radiators; the strength of the dosage.

Considerable variations in the dimensions of the whole apparatus are, of course, allowable, according as special circumstances may require.

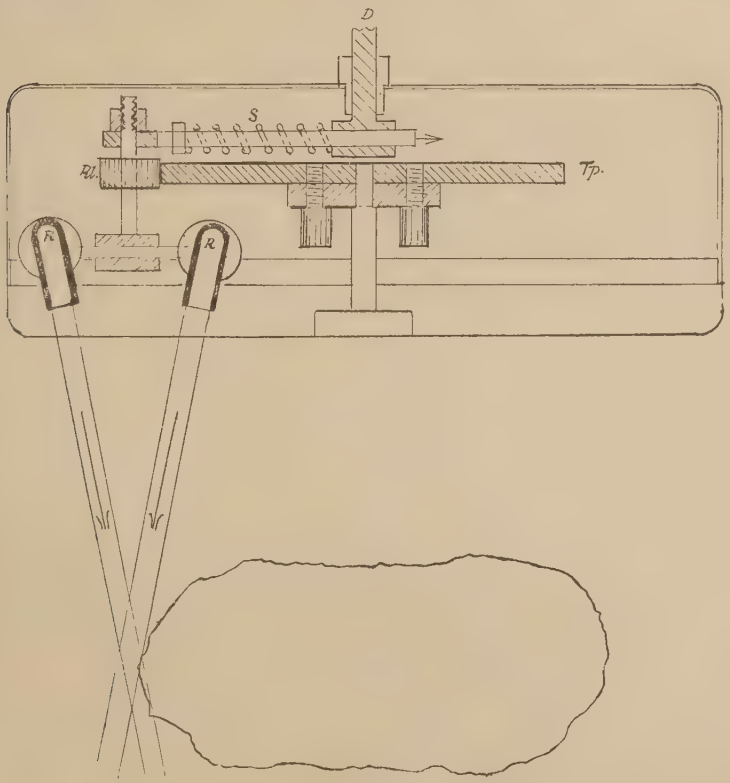
The applicator as depicted is shown in cross-section along a plane which does not reveal covered openings in the flat top of the case, enabling the radiators, etc., to be got at from above, when desirable, without disengaging the roller and template. The mode of applying the drive is also omitted. Preferably this would involve a bevelled toothed wheel attached to the shaft and actuated, through a flexible torsion drive, by clockwork.

In the case when the applicator was worn by the patient the clock-motor would be carried on a light belt; connection with the applicator being made through the flexible torsion drive.

As regards the "efficiency" of the foregoing system of application, it is to be remembered that in any mode of application—save that involving the use of buried radium—one half the radiation is necessarily lost. A flat applicator applied directly to the surface will utilise nearly half the radiations. In order

to secure this efficiency most nearly in the case of the proposed system, the use of a rotating flat applicator, just as much tilted as to secure the "conical" effect, may be used. Of course two such applicators may be brought into operation, coupled as in the figure.

In this case, however, the focus will not be so definite nor so rich in rays as in the arrangement shown in the figure, where a sharper and stronger focus is secured over a lesser area. The increased density of radiation is here brought about by concentrating the radium, so that a deeper layer feeds the beam directed towards the tumour. These advantages are secured at a loss of "efficiency"; as much of the radiation is directed laterally, which, of course, does not reach the patient.



The considerable radium charge required to secure adequate gamma radiation is a source of serious practical limitation to the use of the foregoing system of gamma-ray therapy. Dr. Walter Stevenson suggests a simple way of surmounting this difficulty, which in many cases would involve no special provision. He suggests that the radiators should be given such dimensions as

would enable the platinum radium-cells, ordinarily used in needles, to be used as the source of the rays. Thus, if the internal dimensions of each radiator be 25 × 7 mms. some 24 or 25 radium-filled platinum cells, each carrying one milligram of radium, would fit into each radiator; the external dimensions of these cells being 15 mms. in length, and 1 mm. in diameter. These cells possess walls 0·2 mm. thick. They would, therefore, intercept much of the beta rays. In order to fully charge two radiators the temporary allocation of the charges of some fifty radium-filled needles would be required.

For further screening the opening at the base of each radiator may be closed by a gold, platinum or lead stopper.

No. 38.

A STUDY OF THE POLYSACCHARIDES. PART 2. NOTE ON THE PURIFICATION OF THE NATURAL PRODUCTS.

By J. REILLY and DECLAN T. McSWEENEY, M.Sc.

[Read April 2. Published separately April 24, 1930.]

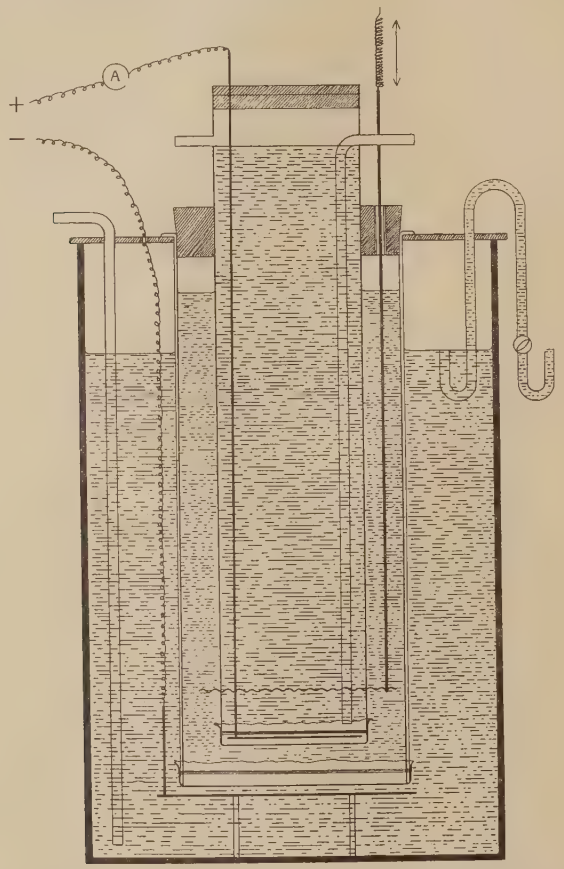
In the investigation of the properties and constitution of natural products, such as the polysaccharides, the purification of materials for analysis and molecular weight determinations is of the utmost importance. In the case of the polysaccharides, the main difficulty is the reduction of the mineral content without drastic treatment of the product or alteration of its chemical constitution. To effect this reduction almost invariably involves several tedious operations. In the literature there are references to the use of electro-dialysis for the removal of mineral impurities. It has been used with success in soil analysis, *e.g.*, Humfeld and Alben, J. Am. Soc. Agron., **20**, 36–50, 1925, and **19**, 984–93, 1927, and in physiological chemistry for the purification of gelatine (Oka, J. Soc. Chem. Ind. (Japan), **30**, 396–402, 1927) and other substances. It has also been applied to the purification of glycogen by Samec and Isajevic (Compt. rend., 1923, **176**, 1419–1421), by Hertzog and Reich (Ber. 1929, **62**, B, 495–499), and Haworth, Hirst, and Webb (J.C.S., 1929, 2481).

The authors have devised a simple apparatus, which may be easily set up in any laboratory, and examined its suitability for mineral reduction with various polysaccharides. It was found to give very satisfactory results, and has been used with success for the electro-dialysis of inulin, glycogen, and mannan. It had also been intended to apply the method to xylan and lichenin, but it was found that the ash content of these after extraction and further purification was negligible. The ash content of the other three was considerably reduced by electro-dialysis.

The electro-dialyser, shown in detail in the figure, consists of two concentric cylinders closed at the bottom with parchment, and immersed in water in a large outer vessel. Simple collodion, albumin collodion, and other membranes have been suggested in the literature, but parchment was found to be quite suitable, and is more readily available. The cylinders were made in sizes, to suit the volume of liquid to be electro-dialysed.

Water was circulated in the outer vessel and the inner cylinder by means of a syphon arrangement, indicated in the figure. Platinum electrodes were placed below the outer membrane and above the inner one. In some preliminary experiments lead plates were used as electrodes. There was no decrease in ash content, and the ash on examination was found to contain lead. Similar trouble was not experienced with platinum plates. Nickel gauze, copper gauze, silver, and gold have also been suggested as electrodes in the literature.

The substance for dialysis was dissolved in distilled water at a convenient and arbitrary concentration, and the solution placed in the annular space between the cylinders. A difference of potential of about 230 volts (taken from the D.C. mains) was applied to the electrodes, and the current passed through for a period of from six to twelve hours. The solution was agitated by means of a glass stirrer, which encircled the inner cylinder, and was raised and lowered by a mechanical arrangement.



The membranes were kept at a distance of four to five centimetres apart. The electrodes were kept as near as possible to the membranes without actually touching them. During the last hour of the dialysis the water in the inner cylinder and outer vessel was replaced by distilled water.

Mannan.—The mannan used was prepared from Salep bulbs. 15 g. of the dried and finely-powdered bulbs were mixed with 2 litres of distilled water and about 20 c.c. of toluol added. The mixture was then shaken for a period

of 48 hours, and allowed to stand. The solid residue was then filtered off, and the filtrate reduced to about 200 c.c. at 15 mm. The aqueous solution of the polysaccharide was run slowly into an equal volume of absolute alcohol, which was kept well stirred. A white precipitate of mannan was formed. This was filtered off and dried, to give a yield of 5 g. On analysis it was found to contain 1·08 per cent. of ash.

2 g. of the above mannan was dissolved in 100 c.c. of distilled water, and submitted to electro-dialysis for a period of 10 hours. The polysaccharide was then precipitated with alcohol, as already described, dried over phosphoric oxide at 80° in vacuo, and the ash determined. The mineral content was found to have been reduced to 0·05 per cent.

Inulin.—Crude inulin from artichokes was purified by solution in water and re-precipitation with alcohol. The mineral content was found to be 0·55 per cent.

5 g. of this inulin was dissolved in 100 c.c. of distilled water and electro-dialysed for 6 hours. The inulin was recovered by concentrating the solution in vacuo and precipitating the product with alcohol.

On analysis the ash content was found to have been reduced to 0·02 per cent.

Glycogen.—The sample of glycogen used was of German origin, from "mies muschel." This was purified by repeated solution in water and precipitation with alcohol. On micro-analysis it gave the following figures:—

5·265 mg. dried at 80° in vacuo over P_2O_5, gave 0·479 mg. loss of weight.

4·786 mg. gave 7·500 mg. CO_2; 2·56 mg. H_2O; and 0·117 mg. of yellow residue.

These figures, calculated on ash-free residue, correspond to: carbon, 42·74 per cent.; hydrogen, 6·9 per cent.; ash, 2·44 per cent.

2·5 g. of this glycogen were dissolved in 100 c.c. of distilled water and electro-dialysed for 8 hours. The solution was concentrated in vacuo, and the glycogen recovered by precipitation with alcohol. On micro-analysis the product gave the following figures:—

4·814 mg. dried at 80° in vacuo over P_2O_5, gave 0·467 mg. loss of weight.

4·347 mg. gave 7·005 mg. CO_2; 2·39 mg. H_2O; traces of residue.

2·827 mg. gave absolutely no trace of nitrogen.

These figures correspond to H_2O 9·7 per cent., C 43·9 per cent., H 6·19 per cent.

$C_6H_{10}O_5 . H_2O$ requires H_2O 10 per cent.

$C_6H_{10}O_5$ requires C 44·4 per cent., H 6·17 per cent.

It is intended to apply this method to the ultimate purification of the two starch components (amylodextrin and amylopectin) in comparison with glycogen, especially in regard to phosphate elimination.

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No. 39.

SOME GEOCHEMICAL APPLICATIONS OF MEASUREMENTS OF HYDROGEN ION CONCENTRATION.

By W. R. G. ATKINS, Sc.D., F.R.S.

[Read February 25. Published separately April 17, 1930.]

Measurements of hydrogen ion concentration have been found to give valuable information in many branches of science, but they do not seem to have been used much in the study of geological problems. The standard work on this subject, "The Determination of Hydrogen Ions," by W. M. Clark (3rd edit., 1928), refers only to its application in the study of calcium carbonate equilibrium by the author, and more extensively by Hastings (1927), as having a geological bearing. In the very extensive bibliography given by Clark, the only title in which geology is mentioned is that of Legendre's (1925) book, of which chapter four, "Problèmes océanographiques et géologiques du pH de l'eau de mer," considers the formation of submarine deposits. No mention of geology is to be found in "Hydrogen Ion Concentration," L. Michaelis, 1926.

In soil science, however, measurements of hydrogen ion concentration have been made for many years past, and an outline of the theory and practice may be found in these Proceedings in the author's paper (1922). Following this up, it was hoped that some applications to geology might have been made, but this was prevented by pressure of work. What follows is rather a brief survey of a possible field of research than the presentation of results.

The solvent action of water has played no little part in the surface history of the earth. Wherever water acts its hydrogen ion concentration is of importance, for its solvent action is largely influenced thereby.

Water dissociates into its ions, between which and the parent substance the usual relation holds:—

$$[H^+] \times [OH^-] = k\,[H_2O] = K_w,$$

for constant temperature. When the ions are present in equivalent amounts, as in pure water, the liquid is said to be neutral. In this condition $K_w = 10^{-14}$, the concentration of each ion being 10^{-7} gram equivalent per litre, or the hydrogen ion concentration being pH 7, where $pH = \log \frac{1}{[H]}$. The degree of dissociation rises (and hence the pH of pure water falls) with rise of temperature, Michaelis having found the value for pure water at 16° C. to be pH 7·10, at 22° C., 7·00, at 28° C., 6·90, falling at 40° C. to 6·71. The magnitude of the change over the relatively small temperature range may best

be appreciated by stating the concentration in non-logarithmic form. Thus, a value $0{\cdot}79 \times 10^{-7}$ g. of hydrogen ion per litre at 16° C. becomes $1{\cdot}59 \times 10^{-7}$ g. at 34° C., viz., it is just doubled, and rises to $1{\cdot}95 \times 10^{-7}$ g. at 40° C., above which determinations appear to be wanting.

Perfectly pure water is, however, an artificial product, never found in nature. Even rain water, collected as it falls, has an appreciable acidity, due to its dissolved carbon dioxide. In a smoky atmosphere sulphur acids may raise the acidity still more. It should be added that, for determining the acidity of unbuffered substances, such as nearly pure water, the indicator method is most suitable, provided only the minimum quantity of indicator be added and that the added indicator is itself not far removed from the *pH* value of the liquid to be tested, so that no appreciable alteration in reaction can be attributed to the reagent.

In the earlier publication (1922) a list of 35 representative samples of natural waters was given. The reaction of natural waters was also considered in its bearing upon the corrosion of metals (1923). In the following table a few typical natural waters are shown, with the *pH* value at air temperature, as determined, using indicators, and Clark and Lubs' standard buffer solutions :—

TABLE I.

The hydrogen ion concentration of natural waters.

SOURCE.	*pH*.	NOTES.
Lake Kawah Idyen, Java, a crater lake in Het Idyen Plateau.	1·5*	Acidity due to sulphur acids.
Water in black peat	4	A little non-volatile acid.
Water in brown moorland peat	4·5	Acid largely CO_2.
Rain in open country	5·9	
Moorland stream (Dartmoor)	6·4	Value increases after each waterfall, as CO_2 is lost to air.
Springs in calcareous regions	6·0–6·6	Varying with relative proportions of calcium bicarbonate and free CO_2.
River water, non-calcareous	6·5–7·0	Also similar lakes.
River water, calcareous	8·0–8·4	Also similar lakes.
Small ponds, among weeds	9·6	During active photosynthesis.
Sea-water, surface	8·1–8·4	High values in the tropics.
Sea-water, in pools	8·6	During active photosynthesis.
Sea-water, 2000 m., Atlantic Ocean	7·95	
Sea-water, 1000 m., Black Sea	7·26	H_2S below 180 m.
Water in alkali soil, Sudan	10·0	Sodium carbonate present.

From the foregoing it may be seen that, as a rule, natural waters lie between *pH* 4 and *pH* 9, the great majority being between *pH* 6 and *pH* 8. Compared with the concentrations used in laboratories these are very low indeed, N/100 HCl being at *pH* 2 and N/100 NaOH at *pH* 12. The low hydrogen ion

* Value kindly communicated by Dr. Olaf Arrhenius.

concentration of natural waters means that many metallic hydroxides are insoluble, or only very slightly soluble, in them. Table II, based mainly on the determinations made by Britton (1925) and others previously quoted (1923), will make this clear. Thus, salts of the alkali metals occur in natural waters, also those of the alkaline earths, calcium and magnesium. Manganous salts could occur, were it not that they get oxidised so quickly to the insoluble manganic condition. The carbonates are less soluble than the hydroxides, but the bicarbonates of the alkali metals are soluble, and those of calcium and magnesium become increasingly so above *pH* 9. In more alkaline solutions the carbonates only exist, and, owing to the removal of CO_2 during photosynthesis, may be precipitated in quantity in the presence of abundant plant life.

TABLE II.

Approximate pH *values for precipitation of metallic hydroxides or basic hydroxides. Initial precipitation,* A; *heavy precipitation,* B.

SALT.	A, *pH.*	B, *pH.*	SALT.	A, *pH.*	B, *pH.*
Ferric	3	5	Chromium	5·5	6
Zirconium	3	4	Zinc	6	7
Stannous	3	4	Lead	6	7·5
Thorium	3·5	5	Rare earths	7	8
Uranic	4	5	Manganous	8 (3·5)	8·5
Aluminium	5	6	Magnesium	10	10·5
Copper	5	6	Calcium	11	12
Ferrous	5·1	7			

One point of great interest emerges from a study of Table II—the difference in the *pH* limits for the precipitation of ferrous and ferric salts as hydroxides. That this is the basis of the continued corrosion of iron by a very small amount of acid has already been explained (1928). It also seems to afford an insight into the mechanism of the formation of certain iron ore deposits, and of their distribution in more or less the same region as coal beds. In nature, on the earth's surface, ferrous salts in solution tend to become oxidised to the ferric condition. It is only in the presence of a large amount of organic matter that one can have a sufficiently great acidity appreciably to dissolve ferric oxides, but the process is rendered all the easier as the organic matter also reduces the ferric to the ferrous state, and removes the oxygen, which would reverse the process. In making the statement concerning the occurrence of the iron in solution and a high acidity we may omit from consideration those special and relatively localized conditions in which sulphur acids are present. Thus, we see that ferrous salts, which are not entirely precipitated even at *pH* 7, can be transported in appreciable quantity in solution in natural waters, whereas ferric salts cannot. Hence it arises that only in the presence of much organic matter are the conditions favourable for the solution of iron, as hydroxide, or

possibly as bicarbonate. When the percolating iron solution reaches a depth in the earth at which it encounters alkaline water, the iron salt must be deposited, or a mere rise in temperature would suffice to decompose the bicarbonate. If the foregoing remarks only sketch in outline the conditions for the deposition of such iron ores as owe their accumulation to transport by water, it seems certain that no full discussion of the matter can leave out of consideration these fundamental relations of the ferrous and ferric hydroxides.

It is possible, also, that measurements of hydrogen ion concentration may contribute something towards the solution of the problem of dolomite formation, whereby the calcium carbonate of coral reefs becomes replaced by magnesium carbonate, tending to the production of an equi-molecular mixture, 45·65 per cent. of magnesium carbonate, a figure very nearly approached in the deeper portions of the Funafuti boring. A study of the ratio of calcium to magnesium in various algae and marine invertebrates has been made by Lipman and Shelley (1924), and by Clarke and Wheeler (1922). The latter especially review the dolomite problem, and comment upon the fact that it is the calcite-forming algae and invertebrates that become dolomitized, not those which form aragonite. They also point out that the organisms from cold northern waters and from very deep waters are low in magnesia as compared with those from warm regions. In Funafuti they consider that dolomitization comes about through leaching out of calcium carbonate, so that magnesium carbonate increases relatively. The formation of dolomite itself, however, requires that both calcium and magnesium carbonate should exist together in solution in such quantities that they can be deposited in an equimolecular compound without apparently bringing the process to a sudden cessation through the complete removal of one or the other. Now in cold northern sea-water the *pH* value may be close to *pH*. 8·1, at the surface, rising somewhat in summer. In the tropics it is about 8·3, or slightly over. The value falls as one goes deeper, save that among algae it may be higher during active photosynthesis, and may become high enough to precipitate calcium bicarbonate in either fresh or salt water.

In the absence of carbonic acid the solubility of calcium carbonate, calcite, is only 0·0131 g. per litre at 16° C. This corresponds to *pH* 9·01. Using indicators, pure calcite crystals, boiled with water and cooled, were found to be at slightly over *pH* 9·0; with limestone which may contain small amounts of magnesium *pH* 9·2 was reached, whereas after boiling, to remove CO_2 and saturate the solution, the more soluble magnesium carbonate gave *pH* 10·0. Now magnesium is a weaker base than calcium, the oxide giving much the same *pH* value as the carbonate, as the alkalinity is due to the hydrolysis of the latter. Calcium, however, is not precipitated as hydroxide till about *pH* 11, and its carbonate, which produces an alkalinity of *pH* 9, and no more, must be far less hydrolysed than that of magnesium. The high solubility of magnesium carbonate, about 0·1 g. per litre, is in reality a pseudo value, for it hydrolyses so much that the solubility is largely that of the oxide or hydroxide. In the same way strontium and barium are progressively stronger bases than calcium,

their hydroxides are more soluble, and their carbonates less soluble than that of calcium.

But when we come to the bicarbonates, as the carbon dioxide pressure increases it appears that the solubility of calcium becomes more nearly equal to magnesium, so that their disparity tends to vanish as the *pH* value falls. If the requisite data do not exist their determination might be expected to throw light upon dolomitization. Various samples of dolomite shaken with water were found to give *pH* 8·3 after one day, and in time as much as *pH* 9, but not higher, though one might expect a higher value on account of the magnesium content of the rock.

All carbonates, however, do not give rise to an alkaline reaction; a specimen of Norwegian siderite, was found to be acid, *pH* 4·9. Evidently it hydrolyses, like any other iron salt, and the hydroxide, being that of a very weak base, the carbonic acid set free makes the solution acid.

In Table III are shown a series of *pH* measurements carried out upon a variety of basalts. The weathered basalts give acid reactions, due possibly to a surface residue of iron carbonate, possibly to acid silicate. In some the acidity remains high, even after prolonged boiling in distilled water. Usually, however, the acidity is decreased, and the reaction finally becomes alkaline. Irregularities up to 0·1 unit in the table may be disregarded, as the determinations were made with standards of 0·2 units interval, and different indicators were used. The black columnar basalt specimen from Staffa was alkaline from the start. The initial alkalinity of No. 2 was probably due to surface contamination.

TABLE III.

pH *values of basalt specimens.*

Column A, 30 min. in boiling water, then cooled. Column B, as A, stood 3 days in air. C, as B. boiled for 40 min., and cooled. D, as C, stood 3 months in air, then boiled for 4 hours, and cooled. Hard glass test tubes used, no trace of alkali on boiling with water.

No.	ORIGIN OF BASALT.	A	B	C	D
1.	Weathered sphaerulitic basalt, Larne	5·4	5·4	5·4	5·4
2.	Basalt dyke, north shore of Loch Tarbert, Jura ...	7·3	7·05	7·0	7·1
3.	Weathered amygdaloidal basalt, Giant's Causeway ...	5·9	6·8	7·1	7·4
4.	Decomposed basalt, Giant's Causeway, purple and white	5·6	7·0	7·3	7·2
5.	Basalt, Runagal Light, Tobermory	5·7	6·8	7·0	7·2
6.	Basalt, Territoire de Murat-le-Quaire	7·4*	7·2	7·1	7·4
7.	Decomposed basalt, Giant's Causeway, red brown ...	7·0	7·4	7·3	7·6
8.	Columnar basalt, Staffa	8·0	8·3	8·3	8·6
9.	"Marble basalt," brown-weathered surface from stream, Scotland	5·4†	5·4	5·4	—

* Crack in tube might give a little alkali. † No. 9 boiled 1½ hrs. (A), 2½ hrs. (B), 9 hrs. (C).

It is perhaps worthy of note that though one ordinarily regards a basalt as insoluble these *pH* determinations show that the solubility is quite appreciable, and very much greater than that of a good quality resistance glass test tube, such as can now be obtained from several British firms. Distilled water, after boiling in such tubes—or in quartz—has a *pH* value of 7·10 to 7·05 at about 15° C. using brown thymol blue and phenol red as indicators with Clark's standard solutions.

It may be seen, then, that each sort of rock has a *pH* value, which is characteristic for its own variety and degree of weathering. This might serve as an aid to identification, though it could never be a specific test. It serves, moreover, to give a rough idea as to the degree of solubility of various minerals.

Another application of measurements of hydrogen ion concentration in geology may lie in their use in the study of the conditions under which crystals are formed from aqueous solution. Wherry has indicated that the well-known variation in the form of alum crystals may thus be studied. The crystals are octahedral when deposited from strongly acid solutions, cubic when the acidity is reduced. The changes are said to be reversed in sodium chloride. It is probable that many other examples could be found, and if silicates are thus influenced the effects might be of much geological interest.

The author is indebted to Professor J. Joly, F.R.S., and to Dr. L. B. Smyth for kindly supplying him with the specimens tested.

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No. 40.

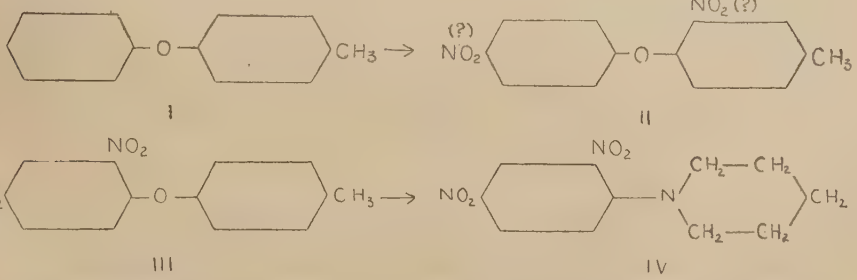
THE NITRATION OF SUBSTITUTED DIARYL ETHERS:— PHENYL-P-TOLYL ETHER.

By JOSEPH REILLY, P. J. DRUMM, and T. GRAY.

[Read February 25. Published separately July 18, 1930.]

The behaviour of di-p-tolyl ether on nitration has been extensively studied by Reilly, Drumm, and Boyd-Barrett (J.C.S., 1927, 671). These authors have found that an almost complete rupture of the molecule takes place, the main products isolated being nitrocresols, accompanied by small amounts of nitrodi-p-tolyl ethers. Nitration in acetic acid gave 2 nitrodi-p-tolyl ether, whilst direct nitration gave 2 : 2′ dinitrodi-p-tolyl ether, thus showing that the oxygen atom is the main orienting influence at work. It seemed of interest to study the behaviour of a diaryl ether in which one phenyl ring is substituted, and phenyl-p-tolyl ether (I) was selected as typical of the class of substance indicated.

The behaviour of this ether on nitration has not hitherto been described. It is now found that as regards decomposition of the molecule by nitric acid with production of nitro phenols, phenyl-p-tolyl ether is intermediate in stability between diphenyl ether and di-p-tolyl ether.



I II III IV

In establishing the constitution of the dinitro compound obtained by direct nitration of the above ether, 2 : 4 dinitro- and 2′ : 6′ dinitrophenyl-p-tolyl ethers have been synthesised, and found to be different from the above. To obtain further evidence of the orientation of the nitro groups in the molecule the method of Turner and his co-workers (J.C.S., 1927, 1168), in which certain nitrodiaryl ethers undergo scission on treatment with piperidine, was employed.

This method, however, has a limited scope of application, piperidine not having any appreciable action on diphenyl ether or its mononitro derivatives. The evidence would seem to indicate that scission by piperidine only takes place readily when 2 nitro groups are present in the same ring. In confirmation of this we have found that 2 : 4 dinitro- (III) and 2 : 4 : 6 trinitro phenyl-p-tolyl ethers are readily decomposed by piperidine with production of 2 : 4 dinitro- (IV) and 2 : 4 : 6 trinitrophenyl piperidine, respectively. Piperidine has no appreciable effect on the dinitration product of phenyl-p-tolyl ether, a fact which would indicate that a nitro group is present in each ring. This result, in conjunction with the well-known directive influence of the oxygen atom, would suggest 4 : 2′ dinitrophenyl-p-tolyl ether (II) as the most probable constitution of the dinitro compound obtained by the action of nitric acid on phenyl-p-tolyl ether.

It was found that the synthesis of 2 : 4 : 6 trinitro phenyl-p-tolyl ether from picryl chloride and potassium-p-cresylate only takes place if the reactants are brought together in cold alcoholic solution. In hot alcoholic solution the main product formed is the potassium salt of picric acid.

Experimental.

Potassium phenoxide (30 g.), p-bromotoluene (31 g.), copper bronze (Naturkupfer C, washed with ether to remove oily impurities) (0·15 g.), and phenol (40 g.) were slowly heated in a flask fitted with an air condenser to 145° C., at which temperature reaction commenced with separation of potassium bromide. Heating was continued for about four hours at 170–180° C. The product, which was dark in colour, was made strongly alkaline, and distilled in a current of steam. Unchanged p-bromotoluene passed over first, followed by an oil of pleasant odour. The latter was taken up with ether, the ethereal layer dried with calcium chloride, and the oil left on removal of the ether distilled. The fraction b.p. 277–278° C. was pure phenyl-p-tolyl ether. (Yield, 75 per cent.) Phenyl-p-tolyl ether is a colourless oil, with an odour resembling geranium. It is readily soluble in benzene, ether, and chloroform, and insoluble in water.

Synthesis of 2′ Nitrophenyl-p-tolyl Ether.

3 nitro 4 bromotoluene (10 g.), potassium phenoxide (9 g.), phenol (20 g), and copper bronze (0·2 g.) were heated in a flask fitted with an air condenser to 170° C., at which temperature reaction set in with separation of potassium bromide. The mixture was further heated for 3 hours at 190–200° C. The dark-coloured product was extracted with ether, and the ethereal layer washed with dilute sodium hydroxide until the latter was colourless, and then washed with water. The dried ethereal extract was fractionated under diminished

pressure, the fraction of b.p. 224–225°/24 mm. being collected. (Found: N, 6·2 per cent., $C_{13}H_{11}O_3N$ requires N 6·1 per cent.) 2′ nitrophenyl-p-tolyl ether is a yellow oil, which does not solidify in a freezing mixture of ice and salt. It is readily soluble in most organic solvents, and is insoluble in water.

Synthesis of 2 : 4 Dinitrophenyl-p-tolyl Ether.

20 g. of 2 : 4 dinitrochlorobenzene were mixed gradually with 17 g. of potassium-p-cresylate by first grinding small amounts together, keeping the cresylate in excess, and then slowly grinding in additional amounts of the two reactants until all was thoroughly mixed. This reaction, being strongly exothermic, had to be carried out carefully, so as to avoid any risk of the temperature rising to the ignition point of the mixture. Large amounts of the components were not permitted, therefore, to accumulate without being brought quickly into reaction by mixing. Upon the conclusion of the reaction, the mixture was allowed to stand over night, after which it was pulverised under water. The water was then decanted off, and the residue washed thoroughly with dilute caustic soda solution, and finally with water again. The insoluble portion was taken up with alcohol, from which it separated in practically colourless plates of m.p. 93° C. (Found by micro method: 3·158 mg. gave 0·285 c.c. N_2 at 21·5° C. and 746 mm., N 10·3 per cent., $C_{13}H_{10}O_5N_2$ requires N 10·2 per cent.) Yield, 17 g. 2 : 4 dinitrophenyl-p-tolyl ether is only slightly soluble in cold alcohol. It dissolves readily in chloroform, acetone, and benzene. Boiling 20 per cent. caustic soda solution was without appreciable action on the above nitro ether. On addition of piperidine to 2 : 4 dinitrophenyl-p-tolyl ether considerable heat was developed, an orange-coloured solution being obtained. The solution was boiled for a few minutes, cooled, and diluted with water. The precipitated solid was collected, and dissolved in alcohol, from which it separated as bright yellow prisms m.p. 92° C., which were found to be identical in all respects with 2 : 4 dinitrophenyl piperidine. The aqueous extract from above, on acidification, smelled strongly of p-cresol.

Synthesis of 3′ 6′ Dinitrophenyl-p-tolyl Ether.

Potassium phenoxide (3 g.) and 3 : 5 dinitro-p-bromotoluene (3 g.) (prepared by the method of Jackson and Ittner, J. Amer. Chem. Soc., 1897, **19**, 7) were heated in absolute alcoholic solution on the water-bath for 3 hours. The solution assumed a dark brown colour, potassium bromide separating almost immediately. The hot filtrate, on careful addition of water, deposited a colourless solid, which crystallised from dilute alcohol in colourless flakes m.p. 70° C. (Found: N, 10·5 per cent., $C_{13}H_{10}O_5N_2$ requires N, 10·2 per cent.) 3′ : 6′ dinitrophenyl-p-tolyl ether is readily soluble in alcohol, ether, acetone, and chloroform, and insoluble in water.

Synthesis of 2 : 4 : 6 Trinitrophenyl-p-tolyl Ether.

A cold alcoholic solution of potassium p-cresylate (2 g.) was gradually added, with shaking, to a well-cooled solution of picryl chloride (2 g.) in alcohol, a yellow solid separating after each addition of the cresylate solution. The precipitate was collected, well washed with alcohol, then with water, and finally with alcohol. A solution in hot alcohol deposited on cooling yellow needles m.p. 103° C. (Found by micro method: 3·060 mg. gave 0·360 c.c. N_2 at 22° C. and 746 mm., N, 13·4 per cent., $C_{13}H_9O_7N_3$ requires N, 13·2 per cent.) 2 : 4 : 6 trinitrophenyl-p-tolyl ether is readily soluble in acetone, chloroform, and benzene, and sparingly soluble in cold alcohol and petroleum ether. On addition of the above ether in piperidine a considerable amount of heat was evolved, a dark orange solution being obtained. The precipitate formed on addition of water was collected and crystallised from alcohol, when 2 : 4 : 6 trinitrophenyl piperidine was obtained as reddish-orange prisms m.p. 106° C. Addition of a hot alcoholic solution of potassium-p-cresylate to a hot alcoholic solution of picryl chloride gave a red precipitate, which was found to consist exclusively of potassium picrate.

Nitration of Phenyl-p-tolyl Ether in Acetic Acid Solution.

To a well-cooled solution of nitric acid (12 c.c., sp. gr. 1·5) in glacial acetic acid (50 c.c.) was slowly added with stirring phenyl-p-tolyl ether (5 g.). After addition of the ether the freezing mixture was removed, and the temperature of the solution allowed to rise slowly to 30° C., at which stage the reddish-coloured solution was poured on crushed ice. The precipitated oil was extracted with ether, and the ethereal solution washed with sodium hydroxide solution to remove nitro phenols, then with water, and finally dried over anhydrous potassium carbonate. On removal of the ether a dark red oil remained, which was fractionated under reduced pressure. At first unchanged phenyl-p-tolyl ether passed over, and this was followed by a yellow oil, which boiled constantly at 204° C./21 mm. (Found: N, 6·1 per cent., $C_{13}H_{11}O_3N$ requires N 6·1 per cent.)

All attempts to induce crystallisation of the above mononitro phenyl-p-tolyl ether were unsuccessful. The dark red alkaline extract was acidified, and the yellow precipitate formed collected and distilled in a current of steam. From the distillate a small quantity (0·5 g.) of a yellow solid separated, which was identified as 3 nitro-p-cresol by the method of mixed melting point, with an authentic specimen of the latter. The yellow solid remaining after distillation was dissolved in alcohol, from which it was obtained as a yellow crystalline solid m.p. 82° C. A mixture with 3 : 5 dinitro-p-cresol melted at 83° C., with which substance, therefore, it was identical.

Direct Nitration of Phenyl-p-tolyl Ether.

Phenyl-p-tolyl ether (5 g.) was added during 1 hour to nitric acid (10 c.c., sp. gr. 1·51) at $-20°$ to $-10°$. As the reaction tended to become rather violent, external cooling was effected by means of solid carbon dioxide. The resulting dark red solution was poured on to crushed ice. The precipitated oily solid was washed in ethereal solution with dilute aqueous sodium hydroxide until this showed no coloration, then with water, and dried. On spontaneous evaporation of the ether there remained a solid, which, after repeated crystallisation from alcohol, was obtained as faint yellow prisms m.p. 101–102° C. (Found: N, 10·3 per cent., $C_{13}H_{10}O_5N_2$ requires N 10·2 per cent.) From the alkaline extract 2 : 4 dinitrophenol was isolated in the usual way.

The above dinitrophenyl-p-tolyl ether was heated to boiling with piperidine. The residue left on dilution of the orange-coloured piperidine solution with water was found to be mainly unchanged dinitrophenyl-p-tolyl ether. The aqueous piperidine extract on acidification smelled of nitro phenol, thus showing that partial scission of the dinitro ether had taken place. The above dinitrophenyl-p-tolyl ether was found to be different from 2 : 4 dinitro- and 2′ : 6′ dinitro phenyl-p-tolyl ether by the mixed melting point method. It is probably 4 : 2′ dinitrophenyl-p-tolyl ether.

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No. 41.

STUDY OF THE POLYSACCHARIDES. Part III. ACETAMIDE AS A POLYSACCHARIDE SOLVENT.

By J. REILLY, M.A., D. ès Sc., REINHOLD WOLTER, Ph.D.,
AND
P. P. DONOVAN, M.Sc.

[Read April 29. Published separately July 25, 1930.]

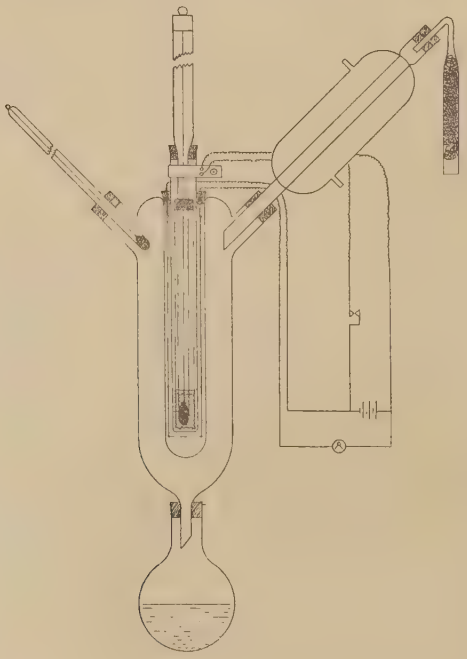
Acetamide at or above its melting point is a solvent for certain polysaccharides, as the authors have recently shown, and from molecular weight determinations it is found that the carbohydrates in solution in acetamide exist as comparatively simple molecules (Pringsheim, Reilly, and Donovan, Ber., 1929, **62**, 2378). In these determinations the value of the molecular depression constant of acetamide was taken as that found by Bruni and Trovanelli (Rend. Accad., Lincei, **13 b**, 176, 1904; Gazetta Chimica Italiana, **34**, ii, 349, 1904; and Bruni and Manuelli, Z. El. Ch. w., 603). With urethane as solute these authors have determined the molecular depression figure of acetamide, and at concentrations varying from 0·9 per cent. to 2·4 per cent. obtained values ranging from 35·5 to 36·4. Using naphthalene as solute in acetamide a constant of 33·3 was determined, which did not alter appreciably with wide variations in concentrations. From observations with concentrations of di-phenyl in acetamide varying from 0·9 per cent. to 2·5 per cent. a figure of 37·3 was obtained as molecular depression constant.

From the above determinations the value of K for acetamide is generally taken as 36·3. With thioacetamide as solute, however, slightly higher values of K were obtained for acetamide, the values ranging from 38·2 to 42·3, depending on the concentrations. These results, however, were regarded as being due to dissociation phenomena.

In our earlier experiments on the determination of the cryoscopic constant of acetamide we employed water in the outside bath, which was kept at a temperature of 3° C. lower than that of the melting point of acetamide. Some difficulty was experienced in keeping the temperature constant, and in a modified apparatus the water has been replaced by ethyl alcohol, which at boiling point gives the required temperature. The modified apparatus is shown

in the sketch.[1] In the first apparatus devised by the authors the heating jacket was constructed of tin as a matter of convenience, but for subsequent work a glass vessel will be used, as this makes it possible to watch the crystallisation of the molten acetamide, and the dissolving of the added substance. The glass vessel was made to our design by the Manchester Scientific Glassblowing Company.

The general procedure followed was as described in "Physico-Chemical Methods" (Reilly, Rae, and Wheeler, pp. 424–425), allowance being made for



the fact that a hygroscopic substance (acetamide) with a much higher freezing point than water was used as a solvent.

The melting of the acetamide, which was previously vacuum-dried in a vessel surrounded by alcohol vapour, was effected by raising the temperature of the water in the bath to about 85° C., and then cooling to 78° C. In the new apparatus a device was adopted of inserting a small resistance wire between the two tubes. The acetamide was then melted by electrically heating this wire. In this way the temperature of the heating jacket was kept constant, while

[1] The authors wish to thank Dr. T. Donnelly for this sketch of apparatus.

the melting of the acetamide was accomplished without removing the inner tube after each reading.

In a recent paper (Ber., **62**, 3078, 1929) by Freudenberg on the molecular weight of triacetylcellulose in acetic acid some remarkable results were obtained in experiments at small concentrations, depending upon the procedure employed in the molecular weight determinations of polysaccharides and their depolymerised derivatives. He states that certain low results obtained for molecular weights depended on the degree of super-cooling and the delayed speed of crystallisation. This is of special importance when small depressions are produced by solution of polysaccharides or non-crystalline substances in the solvent (cf., Standinger and others, Ber., **61**, 2575, 128, 1928, on molecular weight of rubber solutions, who also observe delayed crystallisation of solvent). Freudenberg uses the following method:—When melting the crystals of the solvent (*e.g.*, acetic acid) which separate during the molecular weight determination in the cryoscopic method, he raises the temperature only 0·8° to 1° over the melting point of the acetic acid. In this way a few small crystals of the acetic acid remain unmelted. The temperature is then lowered by the cooling of the outer jacket until the thermometer reads from 0·05° to 0·1° above the melting point of the acetic acid. Stirring is then commenced by means of the "make and break" device. In this way the degree of under-cooling does not go below 0·08° to 0·1° before the mercury thread ascends, and crystallisation of the solvent begins. If the under-cooling is greater than the above limits, the mercury will register a higher figure, owing to the fact that a large number of small crystals (with a corresponding larger surface) are formed, and these serve as a quick-heat supplier ("gute Wärme-Nachlieferung"), and, therefore, the mercury rises more quickly. On the other hand, if the degree of super-cooling is less than the above limits the mercury will give a lower reading, as in this case fewer big crystals will be formed, thereby lessening the heat supply, and thus slowing down the rise of the mercury. In consequence, a very long time is required to reach equilibrium. The temperature of the outside bath, of course, also affects the speed of crystallisation, since the degree of super-cooling is largely dependent on this external temperature.

The period from the time when the mercury starts to ascend until it reaches its maximum point should be the same in the case of the solvent alone and with the polysaccharide in solution. The same procedure is adopted with the solute in solution as that in the case of the blank or control.

As a result of these observations Freudenberg disputes certain results obtained by Hess in regard to molecular weight determinations of triacetylcellulose in acetic acid. Hess (Ber., **65**, 526, 1930) states, however, that determinations are only influenced when the depressions produced by the solute are of a very small order. He attributes the differences in observations by Freudenberg to the following two facts:—(1) Freudenberg's acetic acid used had not been purified to such an extent as his solvent; (2) the small under-

cooling got by Freudenberg lowers the speed of crystallisation, and thereby gives a bigger depression than the actual solute produces.

We have carried out a large number of molecular weight determinations with various depolymerised polysaccharide products and their acetates, using both the older method and the modified method of Freudenberg. The observations were carried out as far as it was practically possible in a room of constant temperature. With concentrations varying from 0·5 per cent. to 2·5 per cent., both methods gave the same results, within experimental error. Apparently, therefore, at the usual concentrations employed in our work the possible errors referred to by Freudenberg regarding the delayed crystallisation of the polysaccharide has not any appreciable effect on the final reading of the mercury.

In the determination of the molecular depression constant of acetamide described below, Freudenberg's method has been employed, using the modified apparatus. In view of the fact that in our work polysaccharide solutes are used, it was considered advisable to employ substances somewhat akin to the carbohydrates as solutes — cane sugar and mannite were considered suitable substances, and, as a different type of solute, acetanilide and naphthalene were also used. While these substances, being crystalline and of low molecular weight, would probably be very little influenced by super-cooling effects, it was considered advisable to use this method, as in subsequent work substances of high molecular aggregation will be employed as solutes, which in dilute solutions may be influenced by this hesitancy in crystallisation. A series of similar experiments was also carried out with mannite, cane sugar, and acetanilide, using the older method with the modified apparatus, and in each case a close agreement was obtained. There is one distinct difference in the use of acetamide compared with acetic acid. With acetamide the under-cooling is always higher than with acetic acid, and in our experiments the under-cooling is generally 0·2° C. In the older method the under-cooling averages 1° C. or more.

The following examples illustrate the results obtained in determining the molecular depression constant for acetamide, using Freudenberg's method. As is usual in molecular weight determinations, the first reading after introducing the substance is generally abnormal, and is omitted in calculating average values :—

1. *Cane sugar* (*low concentration*).

0·1300 g. Cane sugar, 16·94 g. Acetamide, concentration 0·767 %, make and break about 60 per minute.

Lowest reading on undercooling.	Reading.	Time.
3·38°	3·154°	6 min.
3·37°	3·155°	5 „
3·32°	3·153°	6 „
Average	3·154°	

Lowest reading on undercooling.	Reading.	Time.
3·57°	3·257°	6 min.
3·65°	3·245°	7 „
3·64°	3·246°	8 „
Average	3·245°	
	− 3·154°	
	Δ = 0·091°	

$$K = \frac{M \times \Delta \times W}{w \times 100} = \frac{342 \times 0{\cdot}091 \times 16{\cdot}94}{0{\cdot}1300 \times 100} = 40{\cdot}6.$$

2. *Cane sugar* (*high concentration*).

0·3720 g. Cane sugar, 18·51 g. Acetamide, concentration 2·009 %.

Undercooling.	Reading.	Time.
3·47°	3·104°	5 min.
3·32°	3·103°	7 „
		7 „
3·36°	3·103°	6 „
Average	3·103°	

Undercooling.	Reading.	Time.
3·62°	3·370°	5 min.
3·69°	3·362°	6 „
3·67°	3·362°	6 „
3·67°	3·362°	7 „
Average	3·362°	
	− 3·103°	
	Δ = 0·259°	

$$K = \frac{342 \times 0{\cdot}259 \times 18{\cdot}51}{0{\cdot}3720 \times 100} = 44{\cdot}1.$$

3. *Acetanilide* (*low concentration*).

0·1974 g. Acetanilide, 16·34 g. Acetamide, concentration 1·208 %.

Undercooling.	Reading.	Time.
3·55°	3·191°	5 min.
3·50°	3·190°	4 „
3·61°	3·189°	5 „
Average	3·190°	

Undercooling.	Reading.	Time.
4·25°	3·550°	5 min.
4·30°	3·549°	6 „
4·27°	3·551°	5 „
Average	3·550°	
	− 3·190°	
	Δ = 0·360°	

$$K = \frac{135 \times 0{\cdot}360 \times 16{\cdot}34}{0{\cdot}1974 \times 100} = 40{\cdot}2.$$

4. *Acetanilide* (*high concentration*).

0·3686 g. Acetanilide, 17·16 g. Acetamide, concentration 2·148 %.

Undercooling.	Reading.	Time.	Undercooling.	Reading.	Time.
3·29°	3·053°	4 min.	4·09°	3·700°	8 min.
3·23°	3·055°	5 „	4·10°	3·702°	9 „
3·23°	3·055°	5 „	4·06°	× 3·703°	8 „
3·27°	3·056°	4 „			
			Average	3·702°	
Average	3·055°			– 3·055°	
				Δ = 0·647°	

$$K = \frac{135 \times 0{\cdot}647 \times 17{\cdot}16}{0{\cdot}3686 \times 100} = 40{\cdot}7.$$

5. *Mannite.*

0·3702 g. Mannite, 17·53 g. Acetamide, concentration 2·112 %.

Undercooling.	Reading.	Time.	Undercooling.	Reading.	Time.
3·29°	3·030°	4 min.	3·79°	3·532°	4 min.
3·25°	3·025°	4 „	3·80°	3·519°	6 „
3·24°	3·026°	5 „	3·75°	3·519°	5 „
3·40°	3·024°	4 „	3·78°	3·521°	5 „
Average	3·025°		Average	3·520°	
				– 3·025°	
				Δ = 0·495°	

$$K = \frac{182 \times 0{\cdot}495 \times 17{\cdot}53}{0{\cdot}3702 \times 100} = 42{\cdot}7.$$

6. *Naphthalene.*

0·2004 g. Naphthalene, 15·78 g. Acetamide, concentration 1·270 %.

Undercooling.	Reading.	Time.	Undercooling.	Reading.	Time.
3·35°	3·003°	8 min.	3·60°	3·385°	8 min.
3·38°	3·010°	9 „	3·62°	3·384°	8 „
3·49°	3·008°	9 „	3·63°	3·386°	8 „
3·50°	3·010°	8 „			
3·45°	3·011°	9 „	Average	3·385°	
Average	3·010°			– 3·010°	
				Δ = 0·375°	

$$K = \frac{128 \times 0{\cdot}375 \times 15{\cdot}78}{0{\cdot}2004 \times 100} = 37{\cdot}8.$$

With the ordinary method the following results were obtained:—

7. *Acetanilide.*

0·4021 g. Acetanilide, 16·9 g. Acetamide, concentration 2·38 %.
Depression 0·709° ... ... $K = 40{\cdot}2$.

8. *Mannite.*

0·1880 g. Mannite, 20·87 g. Acetamide, concentration 0·901 %.
Depression 0·194° ... ... $K = 39{\cdot}2$.

9. *Naphthalene.*

0·1850 g. Naphthalene, 20·36 g. Acetamide, concentration 0·908 %.
Depression 0·258° ... ... $K = 36{\cdot}3$.

Similar to Bruni and Trovanelli, we find somewhat lower results with naphthalene than with the other substances. For compounds of the nature of the polysaccharides $[(C_6 H_{10} O_5)_n]$ even the extreme values obtained will not alter the value of n appreciably. While the newer method is probably more uniform, on the other hand it takes considerably longer to carry out, and, except for final determinations, the ordinary method (using the improved apparatus) will be adopted.

University College,
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No. 42.

REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1929.

[Read JUNE 26. Published separately AUGUST 13, 1930.]

DURING the year under review 14,730 millicuries of radon were issued. This is the largest quantity ever issued in one year, and is not far from the maximum obtainable from the stock of radium in the Society's possession. At most periods, and especially towards the end of the year, the demand for radon greatly exceeded the supply. As a result of the generosity of numerous benefactors, it has since been found possible to purchase an additional supply of radium. This will be dealt with in the report for 1930.

Mr. V. C. Barry and Mr. C. B. M'Kenna were elected to the two Radium Exhibitions which became vacant during the year. Mr. Barry having resigned his exhibition owing to taking up other work, Mr. G. Stevenson was appointed to fill the vacancy. The following are the reports submitted by users of radon supplied by the Committee :—

REPORT BY OLIVER CHANCE, M.B., B.CH.,

Coombe Hospital.

Two cases of cancer of the cervix uteri were treated during 1929 at the Coombe Hospital.

One was operable. 51·6 millicuries, divided up into one central tube and ten platinum needles, were implanted for eight days.

The second was a border-line case. 54 millicuries, divided up into one central tube and twelve platinum needles, were inserted for eight days.

The first case was examined on 2nd July, 1930. She was symptomless, and no evidence of growth could be found.

A list of questions was sent to the second case on 26th June, 1930. She is symptomless, and has gained 10 lbs. since operation.

REPORT ON RADIUM TREATMENT BY ANDREW CHARLES, F.R.C.S.,

The City of Dublin Skin and Cancer Hospital, Hume Street, Dublin.

Between October, 1929, and March, 1930, we used radium emanations in seven cases of intra-oral cancer. None of these cases could have been regarded as favourable for operation.

Age and Sex.—All male. Average age, 60 years.

Duration of Disease.—The disease was said to have existed for periods of 5 months to 3 years.

Site of Lesion.—Floor of mouth, 2; buccal mucous membrane, 2; roof of mouth, 1; tongue, 1; and lip, 1.

Lymphatic Involvement.—Two cases showed definite enlargement of sub-maxillary, sub-mental, and cervical glands.

General Condition.—The general condition of patients was of very poor standard. Red blood corpuscles, 2,700,000 to 3,000,000 H.B. 50–70 per cent.

Results.—Three of these cases have shown marked improvement in local condition, and up to the present show no sign of return. Two are still under observation, and up to the present have shown no change for better or worse; one has died.

Re lip case, as far as local condition is concerned, the growth has practically disappeared, but glands have increased in size.

Of the remaining cases, two of which were cancer of the cheek, and about 70 years of age, duration of disease in both cases about 6 to 8 months. Both did well under radium treatment. One has reported regularly, and the condition remains satisfactory. The other case has not reported.

One case of malignant right antrum, improved for a time, but rapidly got worse, and patient died.

One case of malignant epithelioma of dorsal aspect of hand was treated by radium with no result, was amputated from elbow joint, and deep X-ray to axillary glands. Cure resulted.

Summary.—The use of radium in the treatment of malignant growth certainly causes diminution and improvement in local condition, but we have found that in nearly all cases further treatment of diathermy and deep X-ray is necessary.

Review of 74 Cases Treated by Radium Emanation.

By Oswald J. Murphy, M.B., B.Ch.

All the cases under review have been treated by emanation procured from the Radium Institute, Royal Dublin Society. It has proved difficult to keep track of quite a number of the patients, and unfortunately a number of very interesting cases have been lost sight of; but only temporarily, I hope. The review covers cases treated during the last two years, and therefore only progress to date can be given.

Rodent Ulcers.—Twenty-seven cases were treated, and all were cures. Screenage as a routine consisted of 2 mm. lead, 2–4 mm. rubber, covered by gamgee, and the dose varied from 800–1,200 mc. hrs. The raised varieties were

given an unscreened application, varying from half to one and a half hours, depending on their density. The only case worthy of further mention was one of a rodent involving side of nose, inner canthus of eye, eyelid, and cheek, the conjunctiva being acutely congested and the eyesight impaired. X-ray treatment had been given for, I think, six weeks without any improvement; area of ulcer, 1½ sq. inches. On account of the recent X-ray treatment, a small dosage was administered, *i.e.*, 20 mc. for 24 hrs. At intervals of eight weeks this was repeated for three further applications. The result was most satisfactory; the ulcer was completely healed, congestion of conjunctiva ceased, and the eyesight returned to normal. No extra screens were used to cover the eyeball.

Twelve cases of *epithelioma* involving the ear, lips, cheek, fingers, abdomen, and leg were treated.

The usual procedure was by needling, combined with surface applications; the needles used were ·5 mm. platinum and 1 mm. silver, and they usually contained from 3–7 mc. per needle. These were left in for 7–15 days, according to size of growth and quantity of emanation at my disposal.

One ear and one lip case had been treated in the country with "plasters." The lip case seems to be cured, but I have lost sight of the ear case, which I did not consider to be progressing at all favourably.

A case reported to have been an actinamicosis was sent to me. Half the cheek and upper and lower lids were eaten away. Eight needles were buried along the spreading border, and left in for ten days; a dose of 4,500 mc. hrs., and finally 47 mc. unscreened, were applied for 45 minutes about four days later. When seen last there was only one doubtful area of activity—over the antrum—and there is question of the bone being involved.

A very delayed reaction was seen in an epithelioma on front of shin. This was a slow-growing, warty tumour, of years' duration, about 4 × 5 inches. 116·5 mc., screened by 1·5 mm. lead and 2 mm. rubber and 1·5 cms. gamgee, was strapped on for four days. Nothing happened for over six weeks, when practically the whole mass started to slough off. When last seen nearly all tumour had disappeared, but there were still three or four small areas discharging; the condition of the very elderly patient is excellent. I had an unfortunate experience with a lady of 96 who had a superficial epitheliomatous ulcer, about 6 inches below the left breast; 2 × 1 inch in area; no palpable glands. With the usual screening, I gave 1,600 mc. hr. dose. In about a month the whole condition "lit up"; the growth rapidly increased in size; glands palpable. I am convinced she was under dosed. Probably she might have done better if I had used a small amount of emanation over a lengthy period, a technique which I now almost invariably employ.

Epithelioma of the Tongue.—I am firmly of the opinion that radium element is preferable to emanation in these cases. Using very much smaller quantities of the salt over long periods leads to far less fibrosis, and adds to the

after comfort of the patient. Mr. Stanford Cade's excellent results and my own experience have led me to this conclusion.

Another point which impresses me is that the tongue should always be irradiated before any other steps are taken. There is always some local reaction, which passes away uneventfully provided lymphatic drainage is not interfered with. Operative procedures for removal of glands either before, at same time, or very shortly after irradiation of growth in the tongue retard progress, and make conditions very unpleasant for the patient, as you very often get very marked swelling of the tongue. Further, I am convinced that surgical removal, at any time, is contra-indicated.

Papillomatous growths on under side of tongue and on floor of mouth usually present no difficulty. I have never needled them, but I use applicators of Kerr, and made to fit accurately. These are removed at night. Silver needles, 1 mm., surrounded by 4 or 5 mm. of Kerr, are most satisfactory, and they are left in for 12–14 hrs. a day for 14–21 days, depending on quantity of emanation and size of growth. As none of my cases were very advanced, 2,000 mc. hrs. was the largest dose given. Ten cases in all were treated, and of these seven had the growth in posterior third of the tongue. To insure complete relaxation, I consider a general anæsthetic advisable. As far as it is possible, working with emanation, I follow the methods of Mr. Cade, *i.e.*, the distribution of the needles and dosage; this involves using, say, 20–30 mc., and it leads to considerable fibrosis more often than not. As far as I can see, there are two ways of avoiding this: one by using heavier screens (which tends to make the needles too bulky), and, secondly, by using smaller quantities of emanation and repeating the application at weekly or fortnightly intervals till requisite dosage is reached.

Of the ten cases treated, one has died, two are not doing well, three are doing satisfactorily, and four seem to be progressing in a most satisfactory manner; it is too soon to speak of cures. Several growths of the tonsil were treated, with excellent results; ·5 mm. platinum needles and the ordinary steel needles have been used with equal success; but, of course, the steel needles were left in only from 8–18 hours buried in the growth, whereas the platinum were left in up to 5 days and buried round the growth.

One case died shortly after irradiation, *i.e.*, inside three weeks. The growth was only about 1 c.c. in size, and he was given a dosage of 600 mc. hr. in one platinum needle. I did not hear what he died of. A growth in middle third of œsophagus was treated by needling the base of the tumour. When last heard of he was doing well, but that was a year ago now.

Carcinoma of Breast.—The cases treated, seven, were really only for secondaries in skin and in axilla and supra-clavicular region. Without exception, these growths have totally disappeared following prolonged surface application, lasting 2–3 weeks, screened by 2 mm. lead, 4 mm. rubber, and 2 cm. gamgee. Dosage varies from 2,000 mc. hrs. over very small nodules up to 8,000 mc. hrs. over large glands. In only one case was there any unpleasant skin reaction.

Cancer of Uterus and Cervix.—Three cases were treated, and all are doing well. The last case treated was an almost inoperable growth, involving cervix and fornices, especially the right lateral. The cervix was difficult to locate, owing to its having been pulled to one side and on account of inflammation.

Two silver tubes, 1 mm. screening and 2 mm. rubber covering, were placed in the cervical canal—12 mc. in each needle; these were left in till a dose of 2,000 mc. hrs. had been given. Surrounding the cervix like a pessary, and irradiating all the tissues around the growth, were placed 48 mc. in six lead tubes, 1·5 mm. screen and 2 mm. rubber. These were left in for five days, giving a dose of 3,800 mc. hrs. Twelve weeks later all traces of the growth had disappeared, and the cervix had resumed its normal position. Only in the posterior fornix was there one doubtful area. Into this was buried a ·5 mm. platinum needle, containing 7·6 mc., for four days; also a silver tube as before was placed in the cervix and left there for eleven days. The patient has only left the home about four weeks.

Two cases of *Goitre* were irradiated. One was an exophthalmic, which was somewhat improved, but she has not come for further treatment. The second was a very advanced malignant goitre, too far gone for operation. She was referred to me by Surgeon Meade for palliative treatment, as her dyspnœa was distressing and at times alarming, and the poor creature was in a continual state of terror.

64 mc., evenly distributed over the whole goitre area, screened by 2 mm. lead and 4 mm. rubber and 3 cm. gamgee, was strapped on and left continually in position for sixteen days. Inside 24 hours, strange as it may seem, all acute attacks of dyspnœa had ceased, and in three days the feeling of tension was less severe. She went home on the seventeenth day, feeling and looking much better. The growth was greatly reduced in size. I am expecting to hear from her shortly.

Cancer of the Rectum.—Only one case has been treated, and one case is at present under treatment.

In the case treated Surgeon Meade removed the coccix to provide access to the growth, which occupied the posterior and lateral aspect of the bowel. 5 platinum needles and 4 silver tubes, containing a total of 58 mc., were distributed round in the growth. Those needles near the lumen of the bowel were removed after two days; the others were left in for nine days. A total dosage of about 4,000 mc. hrs. was given. A longer irradiation would have been administered only the patient was very old, somewhat cachetic, and her white cells fell to 5,000. After ten days an obstinate constipation due to growth was relieved, and the patient at the end of six weeks had put on weight and had a healthier colour. This was in last October, and I have since heard she is doing well. This, however, I am afraid, is only temporary.

Malignant Gall-bladder.—This was an inoperable case, and I was requested by Surgeon Morrin to apply radium over the liver and gall-bladder, with a view to slow up accumulation of fluid in the abdomen. There were also secondaries

in the skin near site of incision. 94 mc., with usual screening at 4 cms., was applied over an area 6 × 5 inches, with the gall-bladder at lower border. Twenty-four hours later nausea, vomiting, and hiccough started, which became somewhat more distressing as malignant cells were destroyed; finally, after five days, I removed the radium. It was reapplied after two days, but the nausea, etc., was too exhausting, so it was finally taken off. Incidentally, the secondaries disappeared, and the abdomen took twice as long to fill.

Radium in Skin Diseases.—A case of granuloma annulare on both hands and knee responded well to small doses of emanation. Seventeen mc. over each of four areas on the hands, usual screenage, for 6 hours, resulted in complete disappearance, not only on the treated areas, but also of the untreated lesions on the knee. A recurrence took place after nine months, and I utilised approximately the same quantity of emanation, but extended the time to 24 hours. The patient has been free for eighteen months.

At present I am treating a case of lupus vulgaris on the cheek; the lesion is about 3 sq. inches in area. Four applications have been given at six weekly intervals, using from 27–36 mc. emanation. The dosage has increased from 640–1,500 mc. hrs., with usual screens. At present there is only one active apple-jelly nodule, over which I have just applied 1434 mc. emanation.

Keloids and Scars.—Five cases have been treated successfully. One in particular, in which the fingers were completely and rigidly flexed, presents at present no disability whatsoever.

In conclusion, I wish to tender my sincere thanks to the Laboratory staff for their kindness and assistance, especially when demands on emanation were heavy.

Report for the Irish Radium Committee (Royal Dublin Society) of Radium work carried out in the year 1929.

By Walter C. Stevenson, M.D., B.Ch., D.P.H.,
Surgeon, Dr. Steevens' Hospital, Orthopædic Hospital;
Radium Consultant, Rotunda Hospital.

Cases Treated with Radium. Total, 271.

List showing number of patients and the conditions treated during 1929:—

Malignant Cases, 163.	
Cancer of Breast	15
Cancer of Axilla	1
Cancer of Uterus (Cervix)	25
Cancer of Vagina	2
Cancer of Clitoris	1
Cancer of Bladder	1
Cancer of Prostate	1

Cancer of Nose and Mouth	44
Palate, 6; *Maxillary Antrum,* 4; *Mucous Membrane Cheek,* 1; *Tongue,* 19; *Floor of Mouth,* 5; *Lower Jaw,* 3; *Tonsil,* 4; *Tongue and Tonsil,* 2.	
Cancer of Naso-Pharynx	3
Cancer of Pharynx	10
Posterior Wall, 2; *Extrinsic Larynx,* 5; *Post-Cricoid,* 3.	
Cancer of Larynx	2
Cancer of Oesophagus	5
Cancer of Stomach	1
Cancer of Rectum	3
Cancer of Ear	1
Cancer of Thyroid	1
Cancer of Branchial Cleft, Neck	4
Cancer of Lip	7
Cancer of Skin	13
Sarcoma	11
Orbit, 3; *Palate,* 1; *Tongue,* 1; *Tonsil,* 2; *Thumb,* 1; *Ilium,* 1; *Thigh,* 2.	
Rodent Ulcer	12

Non-Malignant Cases, 108.

Abdominal Adhesions ...	3	Otorrhoea	3
Arthritis (Gonorrheal) ...	1	Papilloma	3
Angioma	2	*Tongue,* 1; *Gum,* 1; *Larynx,* 1.	
Colitis	1		
Corns	1	Paronychia	1
Croup	1	Prostatic Enlargement ...	1
Cyst (Congenital) ...	1	Pruritis Ani	3
Cystitis	3	Psoriasis	1
Deafness (Oto-Sclerosis) ...	4	Rheumatism	1
Dupuytren's Contraction ...	1	Sciatica	2
Fibrosis Uteri	2	Sepsis	9
Fissure Lip	1	*Acute,* 7; *Chronic,* 2.	
Glioma, Brain	1	Sinus	1
Glands (Scarlatina) ...	1	Sore Throat	1
Glossalgia	1	Spring Catarrh (Eye) ...	1
Goitre (Exophthalmic) ...	2	Tuberculosis	32
Haemorrhoids	2	*Abscess,* 2; *Bone,* 3; *Glands,* 2; *Joints,* 1; *Peritonitis,* 21; *Tubes and Ovaries,* 2; *Scar (Neck),* 1.	
Inflammatory Swelling ...	2		
Injury	2		
Keratosis	2		
Nevus	7	Ulcers	2
Nerve Injury	1	Warts	4
Osteo-Arthritis	1		

During the year 1929 a larger number of cases have been treated by me with radium than in any previous twelve months, and the proportion of malignant to non-malignant cases is 3 to 2, while in other years the cases in each class were about equal.

It is recognized by those who have been using radium for a considerable number of years that the swing of the pendulum is at present in favour of radium treatment for cancer, but it will undoubtedly be some time before there is a general consensus of opinion as to the true value of radium in combating malignant disease. It is obvious that advanced cases of cancer cannot be cured by radium or any other method, though so far it is the best palliative treatment that we know of. In some centres in England, in which they have a much larger supply of radium and radon than is available in Ireland, advanced cases are not treated at all with radium, the supply being reserved more or less for those in whom there is hope of obtaining a cure. This attitude is quite justifiable, provided that the radium is in constant use and never wasted. To obtain this desideratum entails a great deal of extra work and extra handling of radium, and necessitates a considerable expenditure of valuable time for those who carry out the treatment. It appears, however, to be a common practice for a special applicator to be made up for a patient, which is only suitable for that particular patient, who may use it for half the day at a time instead of for 24 hours. It is quite possible that this kind of intermittent treatment may have advantages, but it usually means reserving a particular supply of radium for one patient, say, for a fortnight instead of five or six days. There is another form of radium treatment in which, say, 4 grams of radium, costing £50,000, are collected in an applicator, termed a "bomb," which is particularly wasteful of radiant energy. The "bomb" treatment is on its trial, but the results obtained by it so far are not, I understand, very encouraging. If this is so, it is most probably due to expecting too much from the recuperative powers of an individual whose organism as a whole cannot cope with the shock and damage it causes. Nor is it very obvious why the "bomb" should replace deep X-ray treatment, with which it corresponds in general principle.

With reference to my personal practice in cancer, I have never turned down a patient for radium treatment because he is incurable. Frequently patients have died before I had sufficient radium to treat them, and in some cases I have had to stop treatment because the patient was unfit to stand even a small dose. One is justified in this attitude, I think, because occasionally most gratifying results follow the treatment, and in most cases there is a very much appreciated relief of suffering for the patient, even though it may be temporary. At the same time, I do not hesitate to give patients whom there is a chance of curing the preference. I am convinced that in no centre I have visited is the preferential treatment of cancer undertaken with the idea of improving statistics, their object being rather to do the most good to the most people. If anything can show the belief in the efficiency of radium treatment and, more important,

its limitations, it is this selection, based on confidence in the result of experience. In any case, this is a great advance on the attitude assumed by the majority of the medical profession some years ago, when only inoperable cases were referred for radium treatment.

In this year's report I do not propose to enter into details of the results obtained by treatment, mostly because I have not had an opportunity of following up the majority of cases. Picking out a few known cases would not give a fair summary of the results obtained, and is useless as a guide unless complete details of technique, dosage, etc., are given.

The details of every treatment, whether for malignant disease or benign conditions, are entered on the radium chart, which I described last year, and also on a dose sheet, which I keep for every patient.

My present methods of radium treatment and the dosage do not differ materially from those reported in 1926, where I entered as fully as possible into the technique and dosage in each case. There is, however, one important point of difference, and that is the lengthening of the duration of treatment, and giving approximately the same dose by using much smaller quantities of radio-active material. This applies particularly to radium or radon needles inserted into malignant growths.

The radium element I possess since 1924, 53·93 mgrs. at that time, now about 53·8, is in 6 cells, 5 of which contain about 10 mg. of radium element each, and one 5 mg. I found on inquiry that if I wished to have the contents of one of the strong cells distributed in 10 single 1 mg. cells, the change would cost about £30, and I would have to take the risk myself of any radium that was lost. Since 1928 I am using 12·08 mg. radium element in 12 iridio-platinum cells, which I bury in iridio-platinum needles, with a total screen of 0·7 mm. of iridio-platinum. The great advantage of the weaker needles, in my opinion, is that the prolonged weak radiation is much less severe on the patient's tissues, and results in less local and general shock, and therefore gives the patient's inherent recuperative powers a better chance of doing their work efficiently. After all, it is not a treatment, but a patient's ability to respond to treatment, that is the ultimate criterion of success. When the radium treatment takes about a week or a fortnight, instead of 12 to 24 hours, though the same dose may be given in each case, the margin of safety is much greater in the former. It is somewhat similar to comparing the photographic results with a very slow and a very fast plate, when 10 minutes might not, and 1/10 second might make all the difference in the success of a photograph. Although it is possible to get good results by both methods in my experience, yet the chances of success with the slow method appear to be better, and are understandable for the reasons already mentioned, and because dosage is more fool-proof. In dealing with non-malignant conditions also, quite small quantities of radio-active material, as 2 millicuries, used for several days, will heal up an ulcer better than a short quick dose.

There is no doubt that both technique and dosage play an important part in the success of radium treatment. As is well recognized, the efficient range

of one focus of radium is small; therefore in a growth of any size it is necessary to use a number of foci, the exception being in the cases of the "bomb," where an enormous quantity of radium is employed as a focus at some distance from the part treated to obtain uniform radiation. In ordinary circumstances the dose one is able to give is limited by the area one is able to treat without excessive damage to vital structures. In previous reports I have described my technique for the treatment of cancer of the cervix. For several years I employed a dose of approximately 9 med. or 1,200 mg.-hrs. in each of three areas in the uterine cavity and cervical canal, a total of about 27 to 30 med. or 4,000 mg.-hrs. All the cases treated in this manner were inoperable, but some good results were obtained. Compared to other structures treated, this dose is large for the area and technique, but no untoward effects resulted on account of the uterus being an inert body, which has not to perform any vital function at the time of treatment; and, indeed, the fundus and body of the uterus do not *per se* require radiation, but act as a filter and distance piece to prevent over-exposure of vital tissue in the parametria and neighbourhood, where extension of the disease urgently requires treatment. Recto-vaginal and vesico-vaginal fistulae did not occur as a result of this technique. For the last couple of years I have used a large circular brass box, 4·5 cm. diameter, or smaller boxes of various shapes, containing a number of radium or radon cells round the periphery of the vaginal surface of the cervix. (The circular box has a central hole, 1 cm. in diameter.) The maximum effective radiation from these boxes is at right angles to the uterine cavity, and there is a cross-fire between the two sets of foci of radiation, which results in a much more thorough and efficient treatment of the parametria. The dose given in the vagina is about 20 med., so that the total dose for one treatment, which is usually all that is necessary, is increased from 30 to 50 med. or 4,000 to nearly 7,000 mg.-hours. The results obtained with this technique are more constant and satisfactory than with a smaller dosage, and several cases of inoperable carcinoma of the cervix were apparent clinical cures four months after the one treatment, which lasted from three and a half days to a week. The screening of the radium is at least 3 mm. thickness of brass, and the protection of the rectum and bladder is increased by a heavy brass distension and distance tube, which is retained in the vagina during the treatment. Heavy screening results in more uniform radiation, as it both acts as a distance piece and cuts off the less penetrating Gamma-rays. When treating a recurrence in the vaginal vault and neighbourhood after a Wertheim's historectomy for cancer of the cervix, one can usually only give a comparatively small dose of, perhaps, 10 to 15 med., as there is no uterus to protect the surrounding vital organs. Similarly, when the uterus is so diseased that a tube cannot be passed up the fundus of the uterus by the gynæcologist on account of grave risk of perforating the peritoneal cavity, the dose is limited to one, or at most two, localities in the uterus, with the box in the vagina, so that it is impossible to give a full dose, and one cannot expect, and as a matter of fact one does not get, as good results as when it is possible to

give a full dose at one sitting. In my experience it is difficult to get hospital patients to come back at the proper time for a second treatment, as they are apt to let the disease progress too far before they return, when they find that their symptoms have been relieved. Of the 25 cases treated for carcinoma of the cervix in 1929, 10 were given a satisfactory dose of over 40 mcd. In one the treatment had to be stopped, on account of the mental condition of the patient. In 7 the full dose could not be given, as it was impossible to introduce the tube into the fundus of the uterus, and 7 cases were treated for recurrence after Wertheim's historectomy. From a general review of the above considerations, it can be seen that the results one may expect from radium treatment depend upon how efficiently the diseased area can be radiated without risking permanent damage to vital structures, or a fatal termination owing to the patient's inability to respond to treatment if a big dose is given. All the cervical cases treated were quite inoperable, except two, which were border-line cases.

In cancer of the cervix the consensus of opinion is that it is particularly suitable for radium treatment, as metastases beyond the range of efficient radium treatment do not occur until comparatively late in the disease. Also a diseased uterus has not to function, and its temporary injury does not interfere with a patient's life. The results of radium treatment for cancer of the breast are also usually good, but here one always fears extension of the disease to the cervical glands and into the thorax. The latter condition is particularly liable to occur, and result in a fatal termination, when there has been a recurrence after a radical amputation of the breast.

Naturally, the earlier the recurrence the more likely metastases and the worse the prognosis. To prevent recurrence, prophylactic radiation after amputation of the breast, no matter how apparently successful the operation is, would appear to be a sound practice. If radiation is delayed until there is marked recurrence, the hope of ultimate cure is not good, as there is almost sure to be trouble inside the chest, though this may not be revealed early by X-ray examination. Of the 15 cases of breast cancer treated this year, 8 had recurrences after operation at periods varying from six months to four years. In a ninth the patient was sent to me for prophylactic treatment; there was no actual recurrence, but some suspicious thickening. One patient of over 80 was treated by surface radiation, and it resulted in relief of pain and shrinkage of the malignant mass, but not its complete disappearance, eight months later. In 2 cases I amputated the breast by a modified Halsted's operation, in which I removed the costal portion of the pectoralis major, and cleared out the axilla, where I inserted radium tubes, and about a fortnight later radiated the scar area. One of these has remained free from disease for 20 months. In the other there was a recurrence in the opposite breast. In this connection it is my experience that the heavy uterine dosage of radium by tubes placed in the axilla at the operation is apt to interfere with the lymphatic circulation and to be followed by delay in healing and some œdema of the arm.

During 1929 three advanced breast cases were referred to me as inoperable by Mr. Chance, my colleague in Steevens' Hospital. They each had fungating masses in the breast, with glands in the axilla, and in one glands palpable above the clavicle. Their general condition was bad. One of these, aged 70, I treated by surface radiation, as I considered she was not fit for an anæsthetic. As a result of this treatment, the skin healed up, the tumour decreased and became flattened instead of prominent, and her general condition improved greatly. As the lump commenced to pain her 3 months later, I amputated the breast, and radiated the operation area 10 days later. Now, 9 months later, she remains in good health. There is no recurrence in the operation area, but there is a suspicious thickening in the posterior axillary fold. In the second case, where general condition was slightly better, I amputated the breast and removed the glands from the axilla, and 8 days later gave her surface radiation over the operation area and clavicle. She did very well, but has been lost sight of recently, probably because she had no further trouble. A third case was aged 55. Her general condition was somewhat better, but the local condition of her breast was worse, as she had a septic and foul-smelling cavity, into which an ordinary match-box would fit easily, in the centre of a lump about the size of a grape-fruit. Through this mass I inserted 6 radium needles, 13 cm. long, containing 53·93 mg. of radium in the 2 cm. at the pointed end, pulling them out at various intervals, 2 cm. each time, so as to radiate the whole area by the method described in previous reports (see also "The Rationale and Technique of Combining Operation with Radium Treatment in Cancer," *Lancet*, Dec. 4th, 1926, p. 1158). Two days later I found she was suffering from toxemia, due to a combination of sepsis and absorption of the products of disintegration of cells due to radium treatment. I felt I would put least strain on the patient's recuperative powers by amputating the mass at once, which I did as an emergency procedure, removing the needles at the same time. I did not risk touching the axilla. The patient suffered from considerable shock, due to the radium treatment combined with the operation, and required artificial heat for three days, after which she made an uninterrupted recovery. The stitches were removed and the patient was allowed up in a week after the operation. The skin had healed by first intention, and I did not see a drop of pus. She returned three months later from the country for surface radiation of the whole breast and supra-clavicular region. She looked healthy, had become fat, and neither Mr. Chance nor I could discover any sign of the disease by palpation or X-rays.

In advanced cases of breast cancer, I believe it is of great advantage to eliminate the cancerous mass—especially when it is ulcerated through the skin—and to bring the edges of the skin together so as not to leave a big area to granulate up. This procedure would hardly be justified, or at least the results would be disappointing, if radium were not used about the same time to promote healing, as it appears to do, and lessen the chances of dissemination of the disease. In the skin incision of none of these five cases operated on do I

consider I was with certainty beyond the affected area, and I would have expected recurrence in the scar if I had not used radium very thoroughly.

I do not propose to discuss in any detail the remainder of the cases treated for cancer. A comparatively small proportion of cancers of the nose and mouth have apparently been cured; some have died, but the majority have been lost sight of. It is often possible to heal up the mouth and tongue condition, but to get rid of metastases in the glands is a much more difficult problem. Small cancers of the lip and skin usually do very well with radium treatment, and one gets surprisingly good results with sarcoma if they can be efficiently treated. One patient with sarcoma of the ilium, which partially filled the groin and false pelvis, has remained well for twelve months after the treatment. The mass is considerably reduced in size, there is no pain, and the patient looks well, and is able to do her work. The case of cancer of the stomach is of interest, as I hesitated to give surface radium treatment three months after resection of the lesser curvature of the stomach for cancer. There was some thickening in the region of the operation and recurrence of symptoms, and the prognosis of three months' life was given. I hesitated because radium treatment sometimes takes so much out of a frail patient. The surface dose administered was 1239 med., or about 16,500 millicurie-hours, in front, at the sides and back of the abdomen, in the operation area, at 15 mm. distance from the skin, the treatment extending over a week. When last heard of, nine months after this treatment, the patient's general condition was reported as satisfactory, the improvement being maintained.

As in previous years, I have treated a number of non-malignant cases with radium. Many of these patients have simply been treated as radium has been available, either because the radon has become too weak to be of any use in treatment of malignant cases, or larger doses are used for a few hours, instead of being wasted when there is no cancer patient ready for them. Next to cancer patients, I consider those suffering from tuberculous peritonitis have the best claim, and 21 of these have been treated during the year. One of these was a nurse, who had to keep herself by her profession. When her abdomen was opened by Dr. Davidson at Steevens' Hospital, her pelvic organs and abdominal peritoneum were found studded with tubercles. She also suffered from obstinate constipation. A month after the operation and radium treatment she returned to work against my advice. Seven months after treatment the patient remains quite well, and constipation is no longer a marked symptom.

As in previous years, the most of my radium work has been carried out by radium emanation capillaries supplied by the Royal Dublin Society, which I use in exactly the same way as the 66 mg. of radium element, which are contained in similar capillaries of iridio-platinum. I calculate the dose available for treatment in exactly the same way in both cases, that is, by the amount of radium emanation disrupted during a treatment. Measurement by "millicuries destroyed," besides other advantages, enables one to know at once the cost of each treatment, and

as 3 mcd. is equal to 400 mg. hrs., mcd. can easily be converted into the more cumbersome mg. hrs.

As the Royal Dublin Society intend increasing their supply of radium by public subscription, perhaps it is not amiss in this year's report to point out the value of their pioneer work in distributing radium emanation to the medical profession at a very moderate cost, especially for hospital patients, for the purpose of the scientific investigation of its effect on disease, notably cancer, and for the relief of human suffering. Early in 1914, thanks to the instigation of its present President, Professor Joly, and the expert knowledge and workmanship of its former Registrar, Mr. Moss, radio-active elements were first sealed in small pin-like capillaries in order that the agent might be easily distributed through a malignant growth enclosed in fine hollow needles. The capillary system of radium treatment, first used in Dublin, is now used the world over, and for this the Royal Dublin Society, as pioneers, can claim the credit. It is necessary for us to realize this, as from time to time one sees in the lay press this system spoken of as if it were apparently a startling innovation, when exactly the same thing has been done in Dublin for the last sixteen years. Those who have been cured of cancers, and whose suffering and pain in many other conditions have been relieved by the foresight of the Royal Dublin Society in recognizing the value of this most powerful therapeutic agent, owe the Society a great debt of gratitude. As the collection of radium emanation could not be undertaken by any Irish hospital or medical society, the medical profession here also are in a position to appreciate very greatly the value of their work.

In conclusion, I wish to express my indebtedness to the staff of the Royal Dublin Society's Radium Institute for their courtesy and help when applying for radon. I also wish to thank those who have sent me patients and who have co-operated with me in their treatment with radium, and the resident staff and nurses of Dr. Steevens' Hospital for loyally carrying out the radium work there.

Recent Papers on Radium Treatment published by Writer.

No. 22.—Some Surgical Uses of Radium. W. C. S. Med. Press and Circ., July 28th, 1928.

No. 23.—Post-Graduate Lecture, T.C.D. The Uses of Radium in Medicine. W. C. S. Irish Jour. of Med. Science, November, 1929.

Report on Radium Treatment by C. M. Taylor, M.B.,

House Surgeon, Sir Patrick Dun's Hospital.

1. *Stricture of Oesophagus.*—Mediastinal lympho-sarcoma. Applications: 2 intra-oesophageal; various surface treatments. *Result*—Swallowing much improved. At a later date, died from resp. failure.

2. *Intra-oesophageal Carcinoma.*—Radium inserted into tumour, which nearly blocked tracheae. Died from tracheo-oesophageal fistula.

3. *Lupus.*—Side of nose; ulcer size of half-crown. Also received sunlight. Cured.

4. *Sarcoma of Parotid.*—Improved. Treatment not finished.

5. *Nævus on Neck.*—Insertion of radium needles. Cured.

6. *Carcinoma of Tongue.*—Recurrence. Improved.

7. *Carcinoma of Tongue.*—No improvement.

8. *Malignant Glands in Neck.*—No improvement.

9. *Malignant Parotid.*—No improvement.

10. *Tubercular Peritonitis.*—Improved, but treatment not yet finished.

11. Secondary deposits of carcinoma (scirrhus) in neck, abdomen, groin. Retarded growth.

Report on Radium Treatment by Josephine Walsh, M.B., B.S.,

Resident Medical Officer, Central Hospital, Galway.

On 27th September and 10th November, 1929, 25 mc. tubes and 30 mc. tubes respectively were supplied to this hospital from the Royal Dublin Society's Radium Institute for radon treatment. Dr. Conor O'Malley gives the following report on these supplies:—"2/v/'29.—John Clarke, 18 mc. radium emanations. 24 hrs. in a serum needle, buried in a recurrent growth of middle turbinate. Result: Growth considerably reduced and hæmorrhage ceased. 10/xi/'29.—Same case returned with extension of growth to opposite side and considerable hæmorrhage. Patient bled white. Radium emanation inserted into area of hæmorrhage. Result: All hæmorrhage ceased and patient recovered sufficiently to leave for home. I have not heard from him since." In March, 1929, and on 6th September, 1929, 10 mc. tubes were supplied. They were applied by Mr. O'Malley, F.R.C.S.E., to a sarcoma of a thigh, and are reported as giving a good result.

The Committee feel that this report would be incomplete without a reference to the heavy loss that medical science has sustained through the death of Dr. Maurice R. J. Hayes. Dr. Hayes had treated numerous patients with radon supplied by the Institute during 1929, but his death early in 1930 prevented him from adding further to the series of records and reviews which have for many years formed valuable features of the Committee's reports.

No. 43.

THE RAISED BEACHES OF THE EAST COAST OF IRELAND.

By C. P. MARTIN, M.B., M.Sc.

(Plate 19.)

[Read May 27. Published separately September 23, 1930.]

Part I.

The Present Position of our Knowledge on the Subject.

The early literature on the subject of raised beaches was complicated by the fact that, then, boulder-clay was regarded as a submarine deposit. Observers, therefore, looked for raised beaches at heights up to the top of the boulder-clay. Any flat area within a few feet of sea level was ascribed to marine action, forming a plain of marine denudation. Kinahan (15) describes them as occurring up to 1,000 feet above sea level. The Memoir of the Geological Survey for the Carlingford district also mentions them at heights far above present level. By degrees it was recognised that boulder-clay was a sub-aerial deposit, and that the evidence on which these features were regarded as raised beaches was inadequate. But, even so, it required more time before the mid-glacial sands and gravels were definitely removed from the category of raised beaches.

Coming to more recent times, certain definite raised beaches were recognised as occurring around the British Isles. The first of these was the raised beach of the South of England described by many writers, notably Usher (28, 6). The whole feature along the south coast was described by Prestwich (24). This beach was found to occur on the coast of Yorkshire (16), in South Wales (27), in the Isle of Man (7), on the North coast of France (5), and on the South coast of Ireland (32). It was everywhere found to be Pre-Glacial or Inter-Glacial in time, and was overlain by glacial deposits. Its formation was followed by a period of emergence of the land (7). Its marked features are a very mature, well planed rock platform and a rock cliff, with a rounded summit, indicating subsequent erosion (32). The height of the beach above High Water Mark was found on the South coasts of England and Ireland to be ten feet (32), in the Channel Isles five to eight feet (7), in the Isle of Man at High Water

Mark (7), and at Flamborough Head a few feet above High Water Mark (16). It has not been found so far in Scotland, but lately a fine glacial shore line has been found in Western Scotland at a height of 135 feet (30). This may be the same beach. Another beach was seen at Dunbar at a height of fifty to sixty feet (7), and another at Durham at sixty feet (33). The relationships of these last two beaches to the glacial deposits are not clear. Beyond a hint of the occurrence of the Pre-Glacial beach at Howth and Bray Head (32), it has not hitherto been observed on the East coast of Ireland.

The next beach in point of time that has been described as occurring round the British Isles is the 100 ft. late glacial raised beach of Scotland. This beach is said to extend only around the seaward end of the promontories of the Scottish coast, and to be excluded from the upper end of the Lochs which were occupied by glaciers (7). The exact manner in which this beach ends is obscure. It may end abruptly (29), or may descend to present sea level (7). This beach has not been found outside Scotland.

There is another beach, the 50 ft. of Scotland, also described in the same localities as the 100 ft. beach. It is said to extend further up the Lochs than the 100 ft. beach, but as a separate entity its existence is doubtful (7).

The next beach, in chronological order, is the so-called 25 ft. or Neolithic beach. It has been given this last name on account of the frequent finding of stone implements of the Neolithic age in association with it (4). This beach has been found round the coasts of Scotland and North-Eastern Ireland. In the latter area it has been described in detail as far South as Greenore (4, 11, 18, 19, 20, 21, 22). In these papers the results of much previous work are summarised. South of this point it has been mentioned as occurring at The Murrough, Wicklow (3), Dublin Bay (3, 11, 18), Sutton, Co. Dublin (8), Ireland's Eye (11, 8), Malahide (3), Lowther Lodge, Balbriggan (11, 8), and South of the Boyne estuary (3). But descriptions of it in these localities have not been given, except at Dublin Bay (8) and Lowther Lodge, Balbriggan (8, 11).

This beach is highest in the region of Oban (7), and falls as it is traced outwards from this point. At Oban its maximum submergence is stated to have been slightly earlier than the Azilian period, and in Cumberland and Larne to have occurred in Campignian time (7). From its contained fauna a mean annual temperature 3°–4° F. higher than that now prevailing in the area has been inferred (7, 21). It is regarded as being separated from the period of the late glacial beaches by a time of emergence of the land, as in the Belfast region it is said to be more recent than the estuarine clays of Belfast Lough (18, 7).

All around the South coast of England abundant evidence in the shape of submerged forests is forthcoming that the land once stood at a higher level than at present (25). As a rule there are two submerged forests, an upper and a lower, separated by estuarine clays. These submerged forests have not been found in Scotland except at Aberdeen (7); but the Carse clays lying on top of the boulder-clay, but under the 25 ft. raised beach, seem equally well to indicate

a submergence (13). It has been stated that peat has been found under the sea off the Dublin, Wicklow, and Wexford coasts (3, 9).

These submerged forests and estuarine clays of the South of England have been correlated with the estuarine clays and submerged peat of the Belfast Lough series (18), and, therefore, the submerged forests are older than the 25 ft. raised beach. The latter at Oban has been declared to be Azilian (7), thus making the submerged forests Palæolithic. As a matter of fact, however, they are generally admitted to be Neolithic (14, 17). There is obviously a contradiction here.

From archæological evidence it has been inferred that the Neolithic movements in the British Isles have been submergence in the South and emergence in the North (17). From what has been written above on the correlation of the Belfast and Thames estuarine series it would appear that at the end of Glacial times the whole area stood at a high level, that it then sank while the estuarine series was laid down, and that finally the Northern part of the area rose. It, perhaps, sank a little again, later on (21). Sollas, apparently, saw this contradiction, and suggests that the Oban caves are earlier than the 25 ft. raised beach (26), as it was on the evidence of these caves that the beach was dated as Azilian. Burkitt also sees the difficulty, and suggests that the remains at Oban are really later than Azilian (1). It seems that the only way of avoiding the difficulty is to abandon the dating by stages of human workmanship.

As to the exact dating of the 25 ft. beach, no precise measure can be given. Clement Reid thinks no change in sea level has occurred for 2,500 years (25). Other authorities think South-Eastern England has sunk 8 ft. since Roman times (14). Clement Reid allows from 1,000 to 1,500 years for the submergence of the submerged forests. The Memoirs of the Geological Survey give reason for thinking that the 25 ft. beach at Innishowen was at sea level just before historical times.

All these complicated changes have been shown to be due to two factors. First, as the ice cap of the Glacial age melted, the enormous volume of water tied up in it was released, and the level of the sea rose; secondly, as the ice cap melted, and a great load was removed from the land, isostasy asserted itself, and after an initial lag the land slowly rose. The interplay of these two factors produced the varied results. There was, possibly, also a slight recrudescence of the ice sheet during its period of melting (31).

In this paper an effort is made to trace these various raised beaches along the East coast of Ireland. No section described in the paper has been described before, except as stated above. In all cases the height of the raised beaches was estimated above High Water Mark. The latter was often a difficult plane to determine; but, as far as possible, the upper limit of the Fucus Zone was taken as demarking it. This limit is generally well marked by Pelvetia. In most cases heights were simply estimated, but in others measurements were made to check the estimates.

Part II.

The Post-glacial or Neolithic Raised Beach.

1. *The Carlingford Peninsula.*

The features to be described on the Carlingford Peninsula are:—(1) A large mass of raised beach deposits, occupying the whole apex of the peninsula; (2) a small exposure of the raised beach at the foot of a headland, one mile West of Cooley Point; and (3) an old sea escarpment in the boulder-clay, with a platform of raised beach material at its foot, extending from Giles Quay to two miles East of Bellurgan.

The first of the above features has already been described by Praeger (21), who says the raised beach at Greenore consists of a northward projecting promontory. This is only a partial description, as, in reality, the raised beach is a south-eastern projection, forming a cap to the end of the peninsula. The area around Greenore is simply a small part of this large area. The raised beach extends back on the northern side of the peninsula as far as the junction of the Dundalk–Greenore, Greenore–Newry railways, and on the southern side as far as a point half a mile west of Cooley Point. West of this line boulder-clay occurs, against which the raised beach material is apparently banked. Beneath the typical raised beach material a tough yellow or greyish clay occurs. Good exposures of this clay are visible at Cooley Point and about quarter of a mile further north. The upper surface of the clay is worn smooth, and has many vertical cracks, extending down about six inches, and filled with beach material from the deposits above. At Cooley Point the upper surface of the clay only just rises out of the shingle of the present beach, but further north it rises about 2 ft. higher. Praeger correlates this clay with his Upper Estuarine Series.

The raised beach deposits consist of stratified beds of sand and shingle. The beds vary widely over short distances, and are mainly of fine and gritty sands, the shingle beds being inconspicuous. The highest point they attain is about 14 ft. above H.W.M., and in many places they are overlain by blown sand. Praeger gives a very full list of the fauna of this beach, as compared with which my list is very meagre, and consists of the following species:—*Patella vulgata, Nassa reticulata, Littorina littorea, Littorina obtusata.*

The second feature mentioned above is a small exposure of the raised beach at the foot of a headland about half a mile West of Cooley Point. The sea is now eroding this headland, mainly from its south-western or southern aspect, and has exposed a section, shown in fig. 1.

The raised beach is here resting on an old platform cut in the boulder-clay, and ending landwards in an old sea cliff. The raised beach itself consists of stratified beds of gritty sands and shingle, and yielded only the following species of shells:—*Littorina littorea, Littorina obtusata.*

The upper surface of the boulder-clay platform was worn smooth. Its seaward side was about 2 ft. above H.W.M. The beach deposits resting on it were 5 ft. thick at the seaward side; about 7 ft. thick at the landward side.

The third feature mentioned above was the occurrence between Giles Quay and a point two miles east of Bellurgan of an old sea cliff in the boulder-clay, with a platform of raised beach material at its foot. In places this platform is 100 yards broad; in others it is now completely eroded, and the sea washes the foot of the boulder-clay cliff. The old boulder-clay cliff has been eroded down to a steep, vegetation-covered escarpment, averaging 25 ft. in height over the platform at its base. The level of the platform itself falls as we go towards Dundalk. Its landward side near Giles Quay is about 6 ft. above H.W.M., but near Bellurgan it is only about 3 ft. above it. The raised beach material is fine gravel, and yielded the following shells:—*Littorina littorea, Littorina obtusata, Trochus cinerarius.*

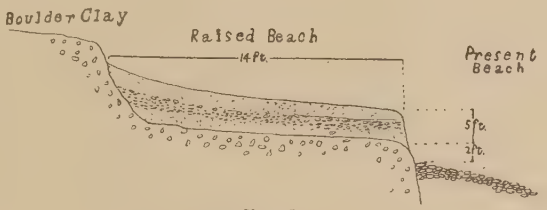

FIG. 1.

RAISED BEACH NEAR COOLEY POINT.

2. *Dundalk Bay.*

The Neolithic raised beach is well developed at two places in Dundalk Bay:—(1) At Soldiers' Point, on the south side of Dundalk Harbour, the raised beach is well exposed in a sand-pit, and beside the road from Dundalk to Soldiers' Point. It consists again of stratified sands and gravels, rising to about 8 ft. above H.W.M. (2) South of Blackrock extensive raised beach deposits occur, and seem to extend for an unknown distance to the west of the Dundalk–Dublin road. Good exposures occur in openings on both banks of the Fane River, and in sand-pits along the coast. It everywhere consists mainly of a stratified sand, but becomes more gravelly inland. At a small farmhouse south of the Fane River, and between the Dublin–Dundalk road and the present beach, a pump was sunk in 1929. Unfortunately I did not see the full exposures, but the farmer told me they went down 15 ft. through gravel and sand with shells. They then came on "a stuff like concrete," about 1 ft. thick, and below this struck a bed of fine loose gravel, with abundant water. Ground level, where the pump was sunk, was about 8 ft. above H.W.M., and was the highest level to which the raised beach material was traced.

This sector yields abundant shells, and the following were identified:—*Cardium edule, Littorina littorea, Mytilis edulis, Gastrana fragilis, Cardium minimum?*

In many places these deposits were overlain by blown sand, and I was unable to find either what lay below the raised beach material or the horizontal extent of the latter.

3. *The Dunany Point—Clogher Head Section.*

Between Dunany Point and Clogher Head is a bay where erosion is at present proceeding rapidly. For the southern half of this bay, a road skirts the coast, and this road has been carried away at many points and repaired with great difficulty. A local inhabitant informed me that her father remembered cornfields on the seaward side of the road. There is a local tradition of an old road that used to run round Dunany Point, and this road is shown on a map of 1845. Not a vestige of it now remains except its blind southern end, running down to the sea near Clogher village.

Openings in the present road and the exposures all along the beach showed the raised beach resting on boulder-clay, which in places forms a miniature cliff at the land side of the modern beach, rising in some places to about 2 ft. in height; in others it cannot be seen. The top of the boulder-clay is smooth, with many small vertical cracks, apparently due to sun action, etc., and on it rests the material of the raised beach—stratified gravel and muddy sand, with shells. Inland, the surface of the country is very low and level, and the raised beach probably extends several hundred yards in breadth. One exposure, however, 100 yards west of the road, showed that the beach material here was more mud and sand, and there may have been a shingle bar standing where the road now runs, and enclosing a brackish tidal lake.

The following shells were found in this section:—*Ostrea edulis, Cardium echinatum.*

Allowing for the considerable recent erosion in this bay, the horizontal extent of the raised beach deposits must originally have been very great.

4. *The Termonfechen Section.*

About a mile south of Clogher Head, the raised beach is again in evidence. Mr. Farrington, of the Royal Irish Academy, drew my attention to this section. The present beach lies at the foot of a low cliff, and at one spot this cliff revealed the following succession:—

Fine sand—possibly blown sand ...	5 ft.
Stratified sand and some shingle ...	1 ft. 6 ins.
Large waterworn boulders	1 ft.
Gritty sand	2 ins.
Boulder-clay	4 ft. (exposed).

The top of the boulder-clay was worn smooth, and had many small vertical cracks filled with sand from the stratum above. The upper six inches in places appeared to have been modified by the sea; the boulder-clay itself was stiff, containing many striated specimens and very large boulders of a green flagstone, very like some of the strata exposed on Clogher Head. It also contained fragments of chalk, flint, and granite pebbles, and some shell fragments. Inland, the level of the top of the platform of boulder-clay fell slightly, but it could only be traced a short distance. A short distance north of the above exposure the material of the raised beach was almost entirely shingle. Traced northwards and southwards, the raised beach sinks into the present one.

Shells were abundant, and of those collected the following were identified:—*Littorina littorea, Littorina obtusata, Nassa reticulata, Cardium spinosum, Venus* sp., *Patella vulgata.*

5. *The Laytown Section.*

South of the Boyne estuary another very good section of the raised beach occurs between Bettystown and Laytown. Due east of the latter place a deep trench had been opened for the purpose of building a wall, at the time I examined it, and good exposures were, therefore, obtainable. The material was bedded fine and gritty sands, with some thin bands of pebbles. The opening extended 2 ft. below the present H.W.M., but the boulder-clay was not visible. The raised beach material extended upwards to about 12 ft. above H.W.M., but the top 4 or 5 ft. are probably blown sand. Shells were abundant, and the following is a list of those identified:—*Mytilis edulis, Patella vulgata, Cardium echinatum, Pecten opercularis, Turritella communis, Buccinum undatum, Littorina littorea, Trochus cinerarius, Littorina obtusata.*

With the exception of the great accumulations of blown sand south of the Portrane peninsula, and again south of Malahide, nothing further of note was found till Howth was reached. Both these accumulations of blown sand probably have a core of shingle, but, if so, it is obscured.

6. *Howth and Dublin Bay.*

These sections are mentioned in the Memoirs of the Geological Survey, and to these I have little to add. They point out that the Peninsula of Howth is connected to the mainland by a shingle bar, which is a part of the Neolithic raised beach, and again a fringe of this raised beach runs round Dublin Bay. The raised beach deposits at Sutton connecting Howth and the mainland must be very deep, as I am informed that the Sutton Sand Company have gone down forty feet without penetrating them. The digging at these pits is done mechanically under water, so the pits are not available for inspection.

South of this area, in Killiney Bay, a submerged forest and peat bed has been seen between tide marks, and has been described by Dr. R. Lloyd Praeger (23).

7. *Bray Head—Wicklow Section.*

From Greystones to Wicklow the railway line runs along a shingle bank, with a marsh on its western side. In places this bank hardly rises at all above the level of the modern storm beach, but in most places it is 4 or 5 ft. above H.W.M. At its southern end the bar terminates in the broad flat turf-covered Murrough of Wicklow. All this bar is part of the raised beach, but where the coast line ran is difficult to say, as on the landward side the marsh mentioned above passes imperceptibly into land. South of Greystones the submerged forest has again been seen (9). I understand that it was exposed for a time during the past winter, 1929–30, and was then seen by Dr. L. B. Smyth and Mr. Stelfox. Immediately north of Wicklow town is a hill known as Church Hill. It is composed of boulder-clay, and is sharply truncated on its seaward aspect, forming a cliff, at whose base runs the Vartry River. At the east side of the river is The Murrough. This cliff apparently represents part of the old coast line. It is practically impossible for it to have been cut by the river, for it is on the concave side of its course.

8. *Wicklow Head.*

Just east of Wicklow Golf Links a small ravine runs down to the sea. Its lower end is filled with boulder-clay, which has a remarkably level top at 8 to 10 ft. above H.W.M., and this surface contains a good number of water-worn pebbles. This may be a remnant of the post-glacial raised beach.

9. *Three Mile Water Bay.*

This bay at present has a fine stretch of sand, backed on the landward side by a belt of sand dunes about 200 yards broad, behind which is an old broken-down cliff of boulder-clay about 35 ft. high. Both north and south of the Three Mile Water River this boulder-clay cliff turns inland at a considerable distance from the river, and forms the sides of a flat-bottomed valley, in which the river runs. North and south of the bay the cliff turns out towards the sea, and lies on the rock of Ardmore Head and Rockfield respectively. At the northern end of the bay, just at Ardmore Head, the boulder-clay has been hardened into calcrete, and three caves have been washed out in this calcrete at about 10 ft. above H.W.M. These caves present all the features of wave wearing, but are now beyond the reach of waves. They are reached by the spray of storms during high tides. As one cave has a cavity, making a pronounced bend round a corner, I conclude that spray could not possibly have caused it. So here we seem to have the most definite evidence that the sea formerly stood at a higher level relative to the land.

The height above H.W.M. of the base of the old boulder-clay cliff inland from the sand dunes is difficult to determine, but I do not think it exceeds 5 ft.

There are other features at this section which, I think, bear evidence of the post-glacial rise of sea level relative to the land. They are referred to later in this paper when dealing with the pre-glacial raised beach.

10. *Arklow.*

North and South of the Avoca River, where the Arklow golf course and Kynoch's works stand, are large areas of sand dunes, backed against a bank masked by sand, and on this bank stands the Golf Clubhouse. Below the clubhouse rock is exposed in the bank.

All this area is apparently part of the post-glacial raised beach, and the bank was the old sea cliff of the former coast line. The elevation of the raised beach in this sector is very small, probably about 6 ft.

South of this area, at the extreme north of Arklow Head, patches of gravel occur just above H.W.M. The locality has been selected for quarrying, and this has largely spoiled any evidence as to the existence of the old raised beach.

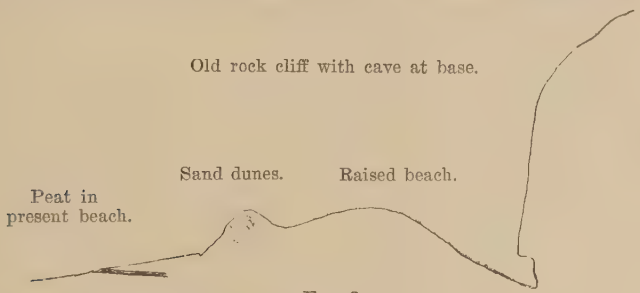

FIG. 2.
DIAGRAM SHOWING SECTION IN BAY SOUTH OF ARKLOW HEAD.

11. *Bay South of Arklow Head.*

South of Arklow Head is a broad bay. It has a sand beach, behind which are some low sand hills. Inland from the sand hills the ground is grass-covered, sandy soil extending inland for about 150 yards, and then, in the northern half of the bay, a sheer rock cliff about 100 ft. high, and in the southern half of the bay a steep bank of boulder-clay. The rock cliff of the northern half joins the cliff of Arklow Head. It agrees with the latter in height, and in its rounded top; in fact, it forms a continuous structure with the cliff of Arklow Head. At the foot of the cliff are two well-marked caves, about 7 ft. high at entrance and 6 ft. deep. In other places heaps of talus and dense vegetation hide the foot of the cliff. At the south end of the bay the boulder-clay bank turns gradually outwards, and joins the present coast line. It is difficult to estimate the height of the base of the cliff above present H.W.M. It does not seem to be more than 2 ft., but about 70 yards out from the base of the cliff the ground is 10 to 14 ft. above H.W.M. The soil is very sandy and covered with fine grass. On the present beach, and about the level of storm waves, a bed of peat crops out from under the sand hills (fig. 2 and Pl. 19). The peat bed

is about 10 inches thick, and the peat very crumbly in texture. Microscopic examination only revealed moss rhizoids and grains of wind-borne quartz.

The sea is at present eroding the land in this bay. At the southern extremity the ruins of a cottage, and beside it the trunk and roots of a large tree, stand out on the edge of the bank, perched above the present beach, and, in addition, the sand hills bordering the beach present everywhere a steep, even, and undercut face towards the sea.

At first sight it looks as if all the features in this bay could have arisen by a gradual silting up, accompanied by accumulation of blown sand, without any change of level occurring. But bearing in mind the evidence of recent erosion in the bay, and in addition the evidence, in the bed of peat now cropping out on the beach, that the land here formerly stood at a higher level, it would appear that the present situation has arisen by the land having once been at a relatively lower level than at present, thus allowing the sea to cut the rock cliff, and then having risen to a relatively higher level, and allowing the peat bed to accumulate, and finally having fallen somewhat to allow of recent erosion.

Wright and Maufe, in their paper on the Pre-glacial raised beach of the south coast, point out that the cliffs of this old coast line can be identified by their rounded tops. As already mentioned, the old cliff inland of this bay has a markedly round top. Further, obviously this rock cliff demanded a considerable period for its creation. Further north, where the post-glacial beach is well developed, we often find a cliff cut in boulder-clay, but nowhere that I know of do we find a cliff cut in rock. The depression of the land causing the post-glacial raised beach appears to have been of too short duration to allow either its rock floor to be planed or a rock cliff cut, at least as far as the east of Ireland is concerned.

E. Hull mentions a cliff cut in mica schist on the post-glacial raised beach in Cantyre, Scotland (12). I have not seen this section, but in view of what I have seen in Ireland, am doubtful if the cliff in question really was cut by the sea of the post-glacial raised beach. In view of all these facts, I conclude that the old rock cliff inland of this bay is pre-glacial in age, and that the post-glacial rise of sea level simply washed out any boulder-clay that had accumulated in the northern half of the bay.

So far as I am aware, this point is the farthest south at which traces of the Neolithic or post-glacial raised beach have been found.

A small raised beach, apparently post-glacial in age, has been described in Tramore Bay, Co. Waterford (7). This may be the recurrence of the Neolithic or 25 ft. beach, but at present I am unable to say.

Part III.

The Pre-glacial or Inter-glacial Raised Beach.

As already stated in Part I, a Pre-glacial or Inter-glacial Raised Beach has been described as occurring along the south coast of Ireland. Wright and Maufe,

who described this beach, worked as far east as Rosslare. My object was to trace the beach northwards along the east coast of Ireland as far as it extended. The essential features of the Pre-glacial Raised Beach, as described by Wright and Maufe, are: a well planed rock platform, about 10 ft. above present H.W.M., overlain by beach material and "Head" and boulder-clay, and backed by an old sea cliff, with a rounded summit.

1. *Section from Wexford Harbour to Cahore Point.*

In this section no solid rock crops out on the present shore. The entire area is covered with vast masses of glacial drift or morainic material, forming one of the terminal moraines of the Irish ice sheet. Professor Charlesworth has mapped this feature (2). Some of the morainic masses near the shore rise above the 100 ft. contour, and are formed throughout of sand and gravel, with fragmentary shells. Any Pre-glacial coast line, therefore, must be deeply buried. Inland of this large moraine nothing was found suggestive of a former shore line.

2. *Section from Cahore Point to Kilmichael Point.*

Between these two headlands the coast forms a very broad bay. Most of this bay has a sandy shore, backed by blown sand, but solid rock occurs on the coast on the northern side of Cahore Point and at several small promontories around the bay, viz., Glasscarrig Point, Rooney Point, Pollshone Head, and Duffcarrick Rocks. On the north side of Cahore Point a much broken platform can be made out. Its inner side was about 10 to 12 ft. above H.W.M., and it then disappeared under a steep bank of boulder-clay.

On the other points named the rock platform was more distinct, and in places was exposed as a very evenly planed surface, disappearing landwards under blown sand or boulder-clay. It is best seen at Rooney Point, where a little gravel lies on the platform. This gravel is apparently derived from the disintegration of the boulder-clay lying on the platform, as patches of gravel occur in the boulder-clay at this locality. Nothing resembling beach materials was found on the platform.

The level of the platform at the apex of each promontory was from 10 to 12 ft. above H.W.M. From the apex of the headlands the level of the platform sank in both northerly and southerly directions, till it reached the level of the present beach at the base of the headlands. It would appear that in pre-glacial or inter-glacial times these promontories consisted of spurs of rock, running out to sea in an easterly direction, and that their upper surfaces were planed into a gently sloping surface by wave action. Boulder-clay was then deposited upon them, and the slope of the now exposed part of the platform from the base of the headlands up to their apices is due to greater erosion having removed more of the boulder-clay from the seaward end of the promontories than from their bases, thus exposing a higher level of the platform.

3. *Kilmichael Point.*

At Kilmichael Point the platform is not visible at the northern side, as it has apparently been completely eroded; but from the apex of the point southwards a very perfect platform appears (Pl. 19). It is bounded landwards by a boulder-clay cliff, about 6 to 8 ft. high, very sheer, and devoid of vegetation. Running through the boulder-clay, and pursuing a very tortuous course, is a bed of peaty material, about 1 ft. thick. It contains many fibres and remains of rootlets. At one locality it seemed to rest directly on the platform, while a little further south about 3 ft. of boulder-clay intervenes between them. It seemingly indicates a break in the deposition of the boulder-clay, but I could detect no variation between the boulder-clay below it and that above it.

The platform is very smooth, terminates in a rock cliff against which the present sea beats, and, like those described above as occurring further south, slopes upwards from the base towards the apex of the headland, where it is about 10 to 12 ft. above H.W.M. No glacial striae were found, nor was any trace found of an old sea cliff terminating the platform on the landward side, and now buried under boulder-clay.

4. *Clogga Point.*

At Clogga Point is a well marked rock platform, presenting features exactly similar to those already described for Kilmichael Point. Nowhere, however, did it seem to attain the same height, its maximum elevation being about 10 ft. above H.W.M. At one point for a considerable distance it was terminated landwards by low sand hills, about 8 ft. high, and in one place below these sand hills was a bed, about 8 inches thick, of a red material, which proved to be grains of quartz held together by ferruginous material. Further south the platform is bounded landwards by a boulder-clay cliff, and here, for a distance of about 200 yards, a bed of fine gravel, about 14 inches thick, underlies the boulder-clay. It contains partly rounded fragments. It is not a typical beach deposit, but is very similar in materials to the calcrete occurring on the south side of Ardmore Head, described further on, but is not so coherent.

South of Clogga Point another small rock promontory runs out to sea, and along its northern side and extremity the rock platform is clearly exposed, but on its southern side it has been completely eroded, and the sea now washes the foot of a rock cliff capped with boulder-clay. The rock platform is exactly similar to that on Clogga Point.

Further south again two small promontories occur, and around them traces of the rock platform can be seen.

5. *Ferrybank.*

About two miles N.E. of Ferrybank, Arklow, a small rock promontory occurs, and round it runs a well exposed platform. It is planed to a very even surface. On the landward side this platform is overlain by boulder-clay; on the

seaward side it sinks to present sea level. The boulder-clay rests directly on the platform, and nothing in the nature of beach materials could be found lying between them; but on part of the exposed portion of the platform large patches of gravel occurred. This gravel, however, could easily be thrown up by present storm waves, as the platform here is low. Measured by using an Abney level, the highest exposed portion of the platform was about 7 ft. 6 in. above the highest point where Pelvetia could be found growing. Measured from the highest wet mark on the sand nearby, the platform seemed to be about 6 in. higher.

Northwards of this point, for about two miles, several small rocky points run out into the present beach, and on most of them traces of the platform can be made out.

6. *Mizzen Head.*

At Mizzen Head (Pl. 19) the smooth rock platform again occurs, but is not complete, as in the north-east extremity it has been completely eroded, and the sea now washes the base of a rock cliff capped by boulder-clay. A large stack stands about 15 yards from the shore at this side of the head, and its upper surface is planed smooth and devoid of boulder-clay, showing that erosion at this point has been rapid since the time of the post-glacial raised beach, and also proving that the platform once extended right round the head. Otherwise the platform is similar to that at Ferrybank. It rises gradually from its northern extremity till it reaches a height of about 14 or 15 ft. above H.W.M., and then slopes gradually to the southern end. On the north side of the head the platform is much broken. On the south-east side it is much more perfect, and about 20 yards broad. On the north side it terminates landwards in a steep bank of boulder-clay, about 30 ft. high; on its south-east face the boulder-clay bank is only about 4 ft. high. The boulder-clay contained some well striated boulders. Exposures showing the platform under the boulder-clay were not available.

7. *Jack's Hole.*

Jack's Hole, which, like Mizzen Head, is covered with boulder-clay, presents on its seaward side a rock platform of similar structure, but not quite so well exposed. The road from Wicklow to Brittas runs along the 100 ft. contour, and is built on rock. The native rock extends in places for about 2 or 3 ft. east of the edge of the road, and then ends abruptly. From that to the sea edge of the old cliff overlooking the rock platform is apparently a deep deposit of boulder-clay. This particular section is very suggestive of a buried rock cliff and platform, but I could get no opening to confirm the surmise. None of the houses east of the road have wells or other openings available for inspection.

At one place 100 yards east of Rockfield House a large pinnacle of rock rises out of the ground. On its north-eastern side the boulder-clay is heaped up to its top. On its southern and western faces it presents sheer rock faces

for about 8 ft., and then disappears into the ground. Possibly this is the summit of an old sea stack, now almost buried. Everywhere else east of the road rock is absent. Borings close to the road would settle the question.

8. *Ardmore Head.*

At Ardmore Head, one mile further north, this feature of a planed rock surface was more noticeable. Running right round this head is a clear-cut rock platform, cut across almost vertical beds of shale and sandstone. Starting at its northern end, it is about 2 or 3 ft. above H.W.M., but as we round the head it rises, till at the apex it is from 12 to 14 ft. above it. From this point it gradually sinks, till at its southern end it again is only 2 or 3 ft. up. The platform varies from 4 to 20 yards broad, is bare of deposits, and covered with lichens. On its landward side it ends in a steep slope of boulder-clay, but at the southern end the boulder-clay has been converted into calcrete, and in this calcrete are three well-worn wave-cut caves at a height of about 10 ft. above H.W.M. (see Part II). The platform was markedly even and mature-looking, with a slight slope seawards (see figs. 3 and 4). In trying to ascertain if the platform extended under the boulder-clay, difficulty was experienced from the fact that the base of the boulder-clay bank represented talus. It was remarked that some of the sandstone beds were cut to a lower level than the shale beds, and, in one instance near the southern end of this platform, it could be seen that this deeper cutting of the sandstone beds did not extend under the boulder-clay. No beach deposit could be found under the boulder-clay. Near its northern end a gigantic granite erratic lies on the even rock platform. No striated rock surface was found. Mr. Farrington has since informed me that he has seen a striated surface at the north end of Ardmore Head. Efforts were made to find any trace under the boulder-clay of an old buried sea cliff, as presumably the rock platform does terminate inland in a rock cliff. No definite evidence was found; but at Three Mile Water Bridge, half a mile south-west of the head, the road crosses a stream where it runs through a narrow gully. Twenty yards east of the bridge the gully is formed of boulder-clay from top to bottom; 100 yards west of the bridge it is formed throughout of solid rock. The height of the top of the gully was in both places the same. Somewhere between these two points the junction must exist, and the junction must be a steep slope or cliff of rock.

9. *The Silver Strand.*

At the Silver Strand, a projecting spur of rock, called the Long Rock, runs out to sea. The very noticeable feature of this rock is that its upper surface has been planed dead even, with a gentle slope seawards. It has neither boulder-clay nor beach material resting on it. It is connected with the mainland by a bed of grey sandstone, which has been almost completely eroded. Its inner end is from 12 to 14 ft. above present H.W.M. It could not be said with certainty whether the platform passed landwards under the boulder-clay or not.

10. *Kilcool and Newcastle.*

Between Rathnew village and Greystones native rock comes to the surface just along the 100 ft. contour. It often rises rather abruptly west of this line, and in some places, notably just east of Kilcool village and half a mile south of Newcastle village, it forms a cliff. East of this line outcrops of native rock are apparently unknown, but the ground is remarkably level, and seemingly formed entirely of sands, gravels, and boulder-clay. The cliff south of Newcastle is especially suggestive. Probably this line of rock cliff, or steeply sloping rock surfaces, represents an old pre-glacial coast line. The level of the bottom of the cliff is, of course, unknown, as it is deeply buried.

11. *Bray Head.*

On the south side of Bray Head a vast sloping pile of boulder-clay has been banked up against the rock. The new railway tunnel built at the southern end of Bray Head is about a mile long. The northern half was cut through solid rock; the southern half through boulder-clay. The junction of the rock and boulder-clay was a vertical plane, the boulder-clay resting against a wall of rock. This wall of rock appears to be the inward continuation of the sea cliff now exposed further to the east, and of course must have been cut before the boulder-clay was deposited. The boulder-clay here cut through was that of the Irish Sea ice, and yielded many shells. I am indebted to Mr. Hinde, the engineer in charge of the tunnel construction, for the above details.

Wright and Maufe, in their paper on the pre-glacial raised beach of southern Ireland, mention that the boulder-clay south of Bray Head was underlain by a rubble, and appeared to rest on a rock platform. I was unable to get any confirmation of these facts. The ground at this particular point is artificial, being part of an old embankment of the D. & S.E. Railway.

12. *Howth.*

The rocky peninsula of Howth is truncated on its landward side by a bold cliff of quartzite at the northern end, and continuous with this at the southern end, where softer shales occur, is a steeply sloping rock surface. This bar runs across from the rhododendron garden south of Howth Castle to just west of the pavilion of Howth Golf Club. Heaped up against this rock cliff is a mass of boulder-clay, forming a steep slope, on which Howth Castle stands, but on both the northern and southern shore the rock surface can be traced out westwards under the boulder-clay.

The rock here is carboniferous limestone and dolomite, and forms a remarkably level platform, on which the boulder-clay rests. The height of this platform is from 2 to 3 ft. above H.W.M., and on both sides of the isthmus it is striated, indicating an ice flow from west to east. The rock ends on the northern shore about 200 yards west of Corr Bridge, and on the southern shore about 600 yards west of the Martello Tower. West of this line is a narrow isthmus, formed of the raised beach which connects Howth with the mainland.

The old quartzite cliff referred to above very probably represents a very ancient pre-glacial coast line. The height of its base is unknown. The platform of carboniferous rocks mentioned as underlying the boulder-clay on both the northern and southern shores may represent the same ancient coast line, but this platform does not extend uniformly into the base of the quartzite cliff, for the carboniferous rocks come to the surface at Corr Castle at a considerably higher elevation.

Wright and Maufe mention that on the south and east sides of Howth the boulder-clay is banked against an old sea cliff, and that at the Lion's Head it is underlain by a rubble similar to that found on the pre-glacial raised beach of the south coast. I was unable to find confirmation of this.

13. *North of Howth.*

Working northwards from Howth, several isolated and small sections appeared, which were suggestive of the pre-glacial rock platform, but none of these are sufficiently definite to warrant description. They simply appeared suggestive in view of the more definite evidence further south. But when we reach the coast of Co. Down, another section worthy of description occurs.

14. *Killough Bay, Co. Down.*

This section is of a somewhat doubtful nature. It probably is a northern extension of the pre-glacial raised beach.

On the south side of Killough Bay, and about 100 yards east of the village of Killough, the old sea cliff in the boulder-clay is on the south side of the road. Between the road and the sea is a mature-looking rock platform. The boulder-clay here is underlain by deposits closely resembling beach deposits; and Mr. Hinch, of the Geological Survey Office, Dublin, who drew my attention to this section, considered that this was a pre-glacial raised beach.

The beds varied greatly over short districts, but at one spot the following was the sequence:—

Cemented boulder-clay	...	...	13 ft., about.
Sand	...	...	6 ins.
Cemented boulder-clay	...	...	2 ft.
Soft sand	...	...	1 ft. 6 ins.
Cemented sand ...	...	...	2 ft.
Cemented sub-angular gravel	...	...	1 ft.
Coarse angular boulders	...	...	Unknown depth.

In the lowest layer some undercutting had taken place, and the sandy layer had been cut into a series of shallow caves, whose floors were about 8 ft. above H.W.M.

At another exposure the section consisted of two broad bands of cemented sand, separated by 2 ft. of cemented sub-angular gravel, and surmounted by about 13 ft. of cemented boulder-clay.

On the landward side of the bay, 100 yards east of the Coastguard Station, is an old sea cave, 6 ft. high and about 8 ft. above H.W.M. The roof of the cave was flat, and composed of a layer of cemented sand, 10 inches thick, above which was a calcrete of cemented sub-angular and water-worn pebbles. The sides of the cave below the sand stratum were composed of a hard pale yellow sandstone.

The old cliff and sea caves at its foot are obviously portions of the post-glacial raised beach; but Mr. Hinch regards the deposits underlying the boulder-clay as being part of a pre-glacial raised beach. None of these beds yielded any organic remains, but he considers this is due to a leaching-out process. However, these beds are exactly similar to those of the mid-glacial sands and gravels elsewhere. The rock platform between the road and sea is, as already remarked, mature-looking, and very similar to the pre-glacial platform occurring in the south. So, on the whole, evidence for regarding this as a pre-glacial raised beach seems slightly uncertain, mainly on account of the wide gap in space between it and known sections of the pre-glacial rock platform, and the absence of any similar features occurring in its own neighbourhood.

The Pre-glacial Raised Beach of the East Coast of Ireland considered as a whole.

Above have been described in detail the sections and features which suggest the existence of a pre-glacial or inter-glacial rock platform and buried sea cliff along the east coast of Ireland.

Wright and Maufe, in their paper on the pre-glacial raised beach of the south coast of Ireland, remark that this beach was characterised by a very mature rock platform, planed down to a very even surface, and bounded on the landward side by a rock cliff with a rounded summit.

The rock platform described above as occurring along the Wicklow coast agrees very closely in its characters of maturity and even surface with that described by Wright and Maufe. The old rock cliff bounding the platform on the landward side has not been definitely identified on the east coast, but certain sections very suggestive of it have been described, *e.g.*, Jack's Hole, Newcastle, etc.; and, apart from marine action, it is practically impossible to account for the platform of the east coast. Although it is at present unknown to what exact height this platform extends, yet it is only along the sea coast that such a feature occurs, so other planing agencies appear to be excluded. Finally, the rock platform occurring along the coast of Co. Wicklow is utterly unlike the platform occurring in north-eastern Ireland in association with the Neolithic or post-glacial raised beach. Good examples of the latter occur along the east coast of the Ards peninsula, and are strikingly immature in appearance. No planing has occurred, but the projecting spurs of rock are simply somewhat rounded. So the East Wicklow platform cannot be due to the post-glacial rise of sea level.

In one respect the East Wicklow platform differs from that described on the south coast, viz., in the absence of beach deposits on the platform. This was probably due, as Wright and Maufe have already suggested, to the fact that on the east coast the direction of ice flow was along shore, and therefore eroded any previous beach deposits, while on the south coast the direction of ice flow was off-shore, and the beach deposits were protected by lying in the lee of the cliff.

The level of the top of the platform above H.W.M. appears to rise as we go northwards towards Ardmore Head. Wright and Maufe give 10 ft. as the height above H.W.M. on the south coast. The level of the platform in East Wicklow appears to be 4 to 5 ft. higher than this. As stated in Part I of this paper, its height in the Channel Isles is 5 to 8 ft., so it rises northwards from the Channel Isles. As stated in the Preliminary Survey of the question, the level of the pre-glacial raised beach in Yorkshire and Isle of Man appears to be at a lower level than on the south coast of Ireland. The rock platform described as occurring on the western side of Howth agrees with the Isle of Man and Yorkshire section in being at a lower level; but some caution is needed here, as it is apparently the seaward end of the platform that is displayed, and the height which its inward end attains is unknown.

At the end of this paper a section at Killough, Co. Down, has been described, which is of a somewhat doubtful nature. It may be the extreme northern end of the pre-glacial raised beach, and it is interesting to note that the section is just within the area of this beach as postulated by Dr. W. B. Wright (Quaternary Ice Age, map, p. 422). Probably, then, the pre-glacial raised beach is highest in Co. Wicklow, and sinks slowly both north and south of this. Another remarkable feature about the platform on the east coast is that the exposures seem to be best in Co. Wicklow, and to be less marked both north and south of this. If this platform is the northern continuation of the pre-glacial one of the south coast, one would expect that the exposures would improve as we go south. But, as already remarked, the height of the platform above H.W.M. seems to increase as we go north from the south coast, at least as far as Ardmore Head. The exposure of the platform in the south coast seems to be due to storm waves of the present sea. As the elevation of the platform rises along the east coast, the exposure of the platform by present storm waves becomes more and more difficult, and here the exposures disimprove. But, by the time the Co. Wicklow coast is reached, we are within the zone of the Neolithic or post-glacial raised beach, and the fine exposures of the pre-glacial platform in this locality are apparently due to erosion during the period of the post-glacial rise of sea level. It is evident that present storm waves could not have washed the boulder-clay off this platform and laid such a broad strip of it absolutely bare, as we find at Ardmore and Mizzen Heads. I have been on the former in very rough weather, and only spray came up over the platform for a matter of 20 yards. This might wash down the boulder-clay to a steep slope, but could not raze it off an almost level platform back to a very steep

escarpment. So, at Ardmore Head, Mizzen Head, etc., I regard the erosion of the boulder-clay off the pre-glacial platform as due to the seas of the post-glacial raised beach (see figs. 3 and 4).

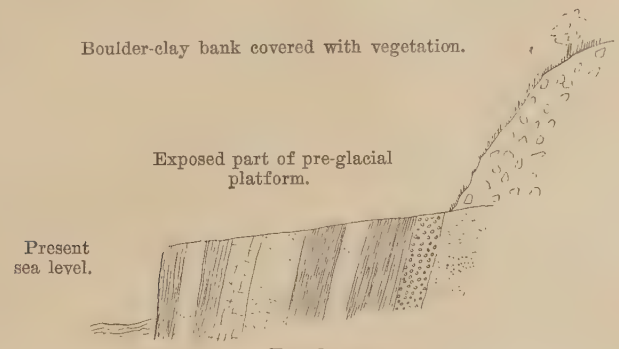

FIG. 3.

DIAGRAM REPRESENTING PRESENT SECTION AT ARDMORE HEAD.

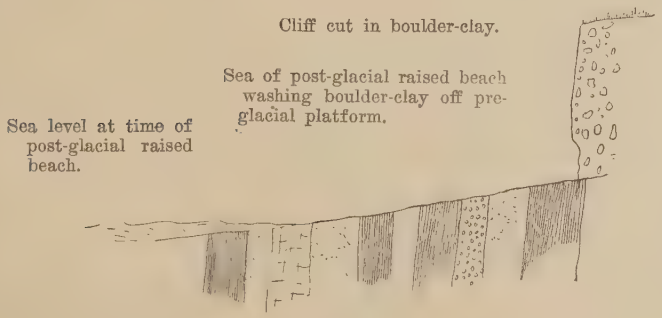
Cliff cut in boulder-clay.
Sea of post-glacial raised beach washing boulder-clay off pre-glacial platform.
Sea level at time of post-glacial raised beach.

FIG. 4.

DIAGRAM SHOWING SUGGESTED POSITION OF SAME SECTION AT TIME OF POST-GLACIAL RAISED BEACH.

CONCLUSIONS.

(1) The Neolithic or 25 ft. raised beach described in the north-east of Ireland extends as far south as the junction of Cos. Wicklow and Wexford, where it sinks to present sea level. The period during which the sea stood at the level of this beach appears to have been short, as no rock cliffs appear to have been cut by it. Its maximum elevation was apparently followed, at least in the southern part of the area, by a slight subsidence.

(2) The pre-glacial raised beach described as occurring on the south coast of Ireland extends round on to the east coast, and as far north as Howth. The raised beach described at Killough, Co. Down, is probably the

extreme northern end of this beach. The height of this raised beach above sea level appears to rise from the south coast northwards to Co. Wicklow, and then to sink again.

I am much indebted to Dr. L. B. Smyth and Dr. R. Lloyd Praeger for suggestions and criticisms while compiling this paper, and to Mr. Hinch, of the Geological Survey, for identifying some of the shells found.

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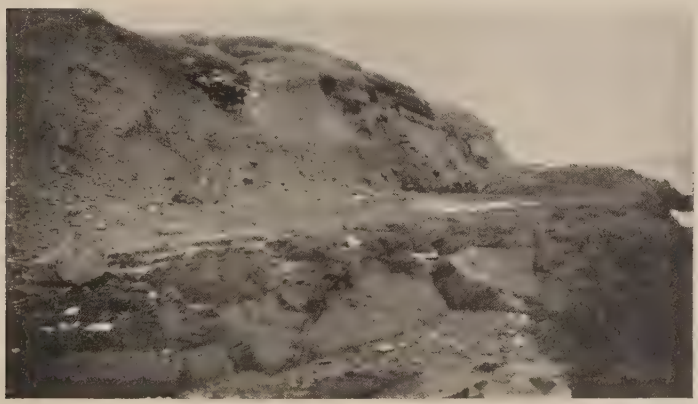
BEACH IN BAY SOUTH OF ARKLOW HEAD. HAMMER IS STANDING IN PEAT BED.



ROCK PLATFORM AT KILMICHAEL POINT.

MIZZEN HEAD.

No. 44.

PAECILOMYCES HIBERNICUM—NEW SPECIES.

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(Plates 20 and 21.)

[Read June 26. Published separately September 11, 1930.]

During the examination of moulds from butter a form was found the species of which at the time was not known, and a detailed study was made of it.

The characteristics are as follows:—

Hyphae fluffy, 3μ in diameter, sparingly septate, sometimes forming cushions reaching to the cover of the Petri dish. Colony at first white; then, when sporing, pink. Undersurface coloured from creamy yellow on nutrient lactose agar, to deep yellow on Potato agar and in Czapek solution. Sporing is very prolific, and the whole growth is soon encrusted with pink conidia, both on the upright and on the trailing hyphae. Later, Isaria-like coremia are formed (Pl. 21, figs. 1 and 2), giving a coralloid appearance.

Fig. 1 shows the low power appearance of a young colony; later the conidia-chains become long and tangled round the aerial trailing hyphae, giving the appearance of fig. 2.

The conidial fructifications are either terminal or on short side branches of the main hyphae, and consist of sterigmata variously arranged, either separate, in verticels, or branching systems resembling a Penicillium head. The sterigmata are very irregular, and of the shape characteristic of the genus Paecilomyces—"Short tubular, or more or less enlarged, tapering into long conidium-bearing tubes, mostly curved, or bent slightly away from the axis of the cells" (1, chap. xxiv). Sterigmata vary very much in the same culture; they may be simple, as described above (Pl. 20, figs. 3 and 5), or may be scarcely distinguishable from conidiophores (fig. 8); again, they may show a series of swellings and constrictions, as in figs. 6 and 7. Conidia are elliptical, 4μ × 2·6μ, at first hyaline, later pink and densely powdering over the mycelium. When grown on mashed potato in a tube there was good growth of white mycellium. Examination of brown areas on the undersurface of the growth showed the

presence of swollen mycelial cells and macrospores similar to those of Horne and Williamson for *Eidamia catenulata* (2).

When cultured in milk there was a felted growth on the surface of the medium and sides of the tube, while the undersurface of the growth was yellow in colour; a soft clot was formed and slowly digested. There was no colour change in calcified milk, but in litmus milk an acid reaction was shown.

After inoculation into Czapek solution and heating to 70° C. in a water-bath, there was no growth of the fungus. When heated to 60° C., however, there was growth. When kept for three weeks at 8° C. in a cold store, the atmosphere of which was kept humid by the presence of brine in open vats, growth was normal; but when kept at 5° C. for three weeks, there was no apparent increase in size of the colony.

When cultured in Czapek solution containing 10 per cent. NaCl, there was growth, but no growth when the Czapek solution contained 15 per cent. NaCl. When 5 per cent. NaCl was present in the Czapek solution, growth was evident in a whitish, gelatinous, submerged film and some thin white scattered surface patches. The hyphae became very septate, and broke into rounded spores, giving an oidium-like appearance. These spores were not observed in the more concentrated NaCl solutions.

When grown in Czapek solution, after four weeks the pH of the medium was 6·4. The original pH of the medium was 7·5.

On gelatine there was very good growth, giving branching, finger-like coremia. The gelatine was partially (50 per cent.) liquefied in 8 days, with small bubbles of gas in the non-liquefied portion, and the reaction was acid (pH = 5).

Diatase production was good.

Paecilomyces Bainer.—Bainer's generic description (1, pp. 541 and 544), translated and amended: "Genus related to Penicillium and Aspergillus, distinguished by sterigmata short-tubular or more or less enlarged, tapering into long conidium-bearing tubes mostly curved, or bent slightly away from the axis of the main sterigmata. Sterigmata variously arranged, partly in verticels and branching systems suggesting Penicillium, partly irregularly arranged upon short branches, partly arising singly along the fertile hyphae; conidia in chains, elliptical, never green.

"Fertile hyphae septate, usually short, mostly creeping, becoming powdery when mature; conidial fructifications either terminal, or on short branches of creeping or partially erect hyphae, consisting of separate sterigmatic cells, of verticels, or of series of verticels of branchlets and sterigmata irregularly distributed along the fertile hyphae; sterigmata with long acuminate tubes, usually bent from the axis of the cell and broadly divergent at the apices, bearing long chains of conidia; conidia elliptical or fusiform."

Considerable confusion exists in regard to the classification of these Paecilomyces forms and their relationship to the Penicillia. Thom (1, p. 545) considers that probably many species referable to Paecilomyces are described by

many authors under the generic names *Corollium, Spicaria, Penicillium, Eidamia* and *Byssochlamys* at least. He advised us, after examination, to place this form as a new species of the *Paecilomyces* group.

Macrospores such as Horne and Williamson (2) described for their *Eidamia catenulata* (placed among the Paecilomyces by Thom) were not observed in our cultures on synthetic medium, but appeared in potato cultures. Swollen cells producing sterigmata were found, however, similar in appearance to those described by the above-mentioned authors in synthetic medium (Czapek). Thom, working on various species, shows how these "specialised cells" vary from the occasional slender stalk and terminal cell (*i.e.*, our fig. 8) to complex structures, as described by Horne and Williamson.

Isaria-like coremia, such as formed in our cultures, have not apparently been reported from other Paecilomyces species. Petch (3), however, mentions Isaria-like coremia formed in culture by a pink *Spicaria* found by Fron on cocoons of *Cochylis* species (*Spicaria* (*Isaria*) *farinosa verticillioides*). This *Spicaria*, which appears to agree with our type fairly well in general description, may be a related form.

SUMMARY.

In examination of moulds from butter a new species of *Paecilomyces* (Bainer) was found, and named *Paecilomyces hibernicum.*

It is a coremia-forming species, with pink spores, clots milk, afterwards digesting the clot, is killed by heating to 70° C., and does not grow in Czapek solution containing 15 per cent. NaCl. It partially liquefies gelatine, with evolution of gas and an acid reaction. Some doubt was entertained as to whether it should be listed under the genus *Paecilomyces* or *Isaria*; but considering its general conidia-bearing structure and the formation of "specialised cells" and macrospores, as previously reported by various authors for species of Paecilomyces, it is included in that genus.

Our thanks are due to Dr. C. Thom, United States Department of Agriculture, Washington, U.S.A., for examining a culture sent to him and confirming it as a new species.

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EXPLANATION OF PLATES.

Plate 20.

Fig.

1. Appearance of young colony under low power.

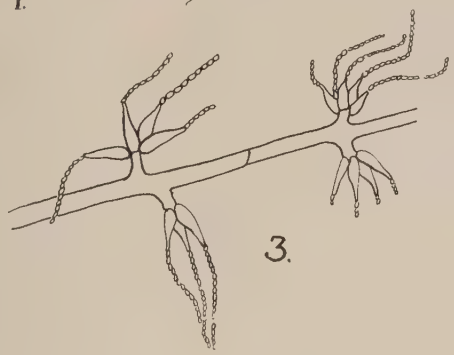
2. Appearance of older colony under low power.

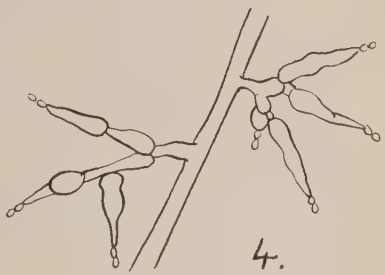
3. Simple arrangement of sterigmata.

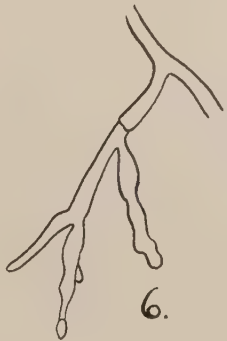
4, 5, 6, 7, and 8. Various types of fructifications, "specialised cells."

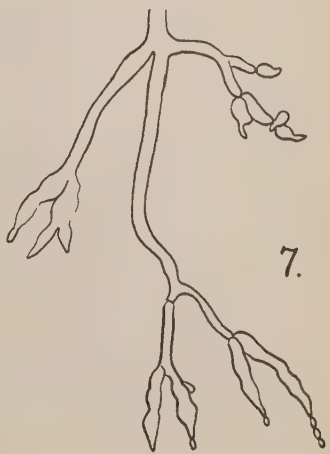
Plate 21.

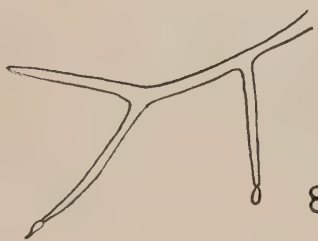
1 and 2. Appearance of coremia in cultures.











PAECILOMYCES HIBERNICUM . n.sp.

V.G.E.R.

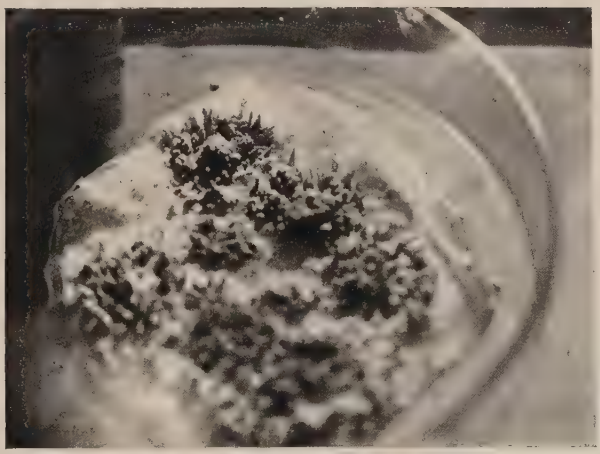


FIG. 1.

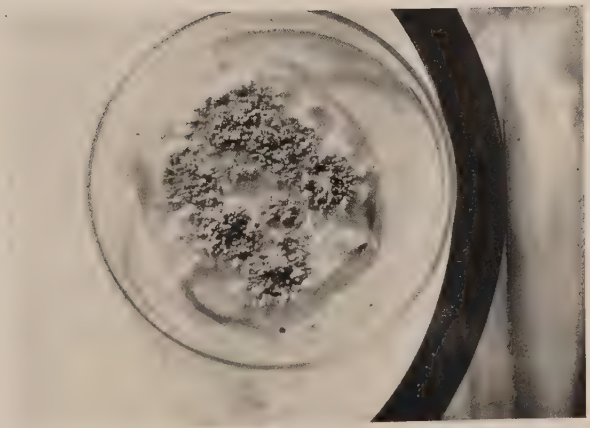


FIG. 2.

No. 45.

PHOTO-ELECTRIC MEASUREMENTS OF ILLUMINATION IN RELATION TO PLANT DISTRIBUTION. PART III. CERTAIN SPRUCE, LARCH, OAK, AND HOLM OAK WOODS.

By W. R. G. ATKINS, Sc.D., F.R.S.,

AND

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[Read May 27. Published separately October 20, 1930.]

Portable photo-electric photometer outfit.

In Part II (1929) a description was given of measurements of illumination made with portable galvanometers. The present work was carried out with this equipment, save that an Onwood micro-ammeter, No. 3140, the characteristics of which were given in Part II, Table 1, was substituted for the lamp and scale galvanometer shown in Fig. 1 of that paper. The outfit proved quite satisfactory for field work over rough ground. The items and their weights are listed in Table 1, those under A being for measurement in the wood, and those under B for use in the open. The total weights are respectively 11·5 and 6·2 kg.; taken together they are less by 3·2 kg. than the equipment carried by a British infantryman in 1914, exclusive of his normal clothes.

Table 1.

Portable photo-electric outfits for field work. A, for work in shaded sites. B, for work in open.

	A.	B.
Dry battery, 60 v.	1·87 kg.	1·87 kg.
10,000 ohm resistance and connections	0·06 „	0·06 „
Micro-ammeter	1·56 „	0·90 „
Photometer with 18 m. (double) cable, A, or 4 m., B ...	2·04 „	0·90 „
Universal shunt, A or × 5 shunt, B	2·35 „	0·34 „
Paraffin wax	0·11 „	0·11 „
Spirit level	0·03 „	0·03 „
Wooden labels for marking positions	0·25 „	0·03 „
Mackintosh sheet, A; "All test" voltmeter, B ...	0·06 „	0·40 „
Cardboard photometer cover	0·06 „	0·03 „
Case, waterproof canvas, A; fibre, B	3·15 „	1·45 „
Total weight, 17·7 kg. ...	11·5 „	6·2 „
39 lbs. 3 oz.	25 lbs. 7 oz.	13 lbs. 12 oz.

The greater weight of outfit A is accounted for by the greater weight of the more sensitive micro-ammeter; by the longer photometer cable, which renders it possible to examine a number of sites without disturbing the micro-ammeter; by the weight of the universal shunt—an item which might possibly be reduced somewhat if specially made; and by the greater weight of the canvas case—a fibre case would be a little lighter in spite of the larger size required for outfit A. Outfit B has probably been reduced to the very minimum of weight possible; the "All test" voltmeter included in it serves for checking the voltage of the A battery also. The weight of A might be better distributed by carrying the universal shunt in a knapsack, which would also permit of the use of a fibre case about the size of that in B. The cases themselves are useful as tables for the micro-ammeters, shunts, and batteries.

The Burt vacuum sodium photo-electric cells used are sensitive only to the blue end of the spectrum. Data concerning the use of a cell sensitive throughout the whole spectrum have been given by Atkins and Poole (1930); it is hoped that Part IV of this series will appear shortly, and treat of such measurements in shaded sites carried out last autumn.

The values of the illuminations, V_s and V_0, in metre candles were obtained as described in Part II, to which reference may be made for a discussion of the optical conditions affecting the measurements and for the methods of stating the results. The constancy of the photometers was tested by frequent cross-checking; they were also checked against a photometer retained in the laboratory and reserved for the purpose.

In the tables, under β, are shown the ratios of the total vertical illumination to the diffuse vertical illumination. The daylight factor, δ, is given as a percentage obtained from $\frac{V_s}{V_0}\beta$, since the light in a wood depends on the diffuse external light only.

Descriptions of the Woods Studied.

Type I.

Evergreen Gymnosperm. *Picea excelsa* dominant.

The first wood was part of a plantation of *Picea excelsa* at Bickleigh, Devon. It is situated on a steeply sloping hill which faces almost due west. The upper limit is bounded by a hedge-bank planted with *Fraxinus excelsior*, and occasional tall and old trees of Fraxinus and Quercus occur with the Picea near this region. The greater part of the plantation, however, is pure spruce. The lower part of the wood terminates sharply on the top of a vertical bank about 1·5 m. high. The trees are planted about 2 metres apart. At the bottom they are approximately 12–15 m. high, and for quite 27 m. from the lower bank inwards there is no undergrowth at all, excepting a few straggling plants of

Hedera helix and *Oxalis acetosella*, the ground being covered with dead spruce leaves. At the upper limits the trees are approximately 9–12 m. high, and the undergrowth is composed of a few bushes of *Corylus avellana* nearly 2 m. high, occasional saplings of *Acer pseudo-platanus* about 2 m. high, with an abundance of herbaceous plants. This growth gradually diminishes from the top downwards, ending somewhat abruptly at a narrow track about 25 cm. wide, which occurs two-thirds of the way down the wood. Below this track the barren condition already described prevails.

Table 2 gives data of the flora of the sites examined inside the plantation, together with the daylight factors for these sites.

The open base was in a field immediately adjoining the hedge at the top of the wood, and figures under V_0 give values of the illumination in metre candles for this position, which was quite unshaded on the top of a hill. Corresponding values for the woodland illumination are given under V_s, and observations were made almost or exactly at the same moment as were those in the open, the observers' watches having been synchronised. The open base photometer was set horizontally with a spirit level.

Base A indicates the first position of the woodland micro-ammeter. This was about 5 m. in from the edge of the lower bank, and well within the barren zone mentioned above.

Base B was about 9 m. above site 11, base A, i.e., well above the barren zone. The slope of the hill is slightly greater here.

Base C was fairly near the top of the wood where the vegetation was good. In all cases the micro-ammeter was roughly levelled with a spirit level, and the photometer, B. 223, which was used for the work in the wood, could be moved about a radius of 18 m. from any given base. All readings were made with the photometer placed horizontally on the ground.

It will be seen from Table 2 that the vertical illumination in the plantation varies from 1·1 per cent. at the bottom to 9·2 per cent. at the top compared with the illumination in the open. In all the sites for base A, the ground is covered by a dense felt of dead spruce leaves, the only growth being a few small plants of Hedera and Oxalis. From outside one has the impression that there is no growth at all under this part of the wood. With δ increased to 2·5, Aspidium seems to grow well, and Rubus appears in stunted trails, producing green fruit at $\delta = 3$, and thriving with ripe fruit at $\delta = 9{\cdot}2$. Small bushes of Corylus appear at $\delta = 3$ and 3·5. Grasses appear rather abruptly at the top with $\delta = 9{\cdot}2$, *Dactylis glomerata* being about 1 m. high. This intensity appears to be sufficient for a variety of herbaceous plants, and the growth of the grasses and of Rubus was dense. Being so near the edge of the wood, the penetration of shafts of sunlight in the forenoon was probably an important source of light. In such situations the maximum, rather than the vertical, illumination regulates the distribution of plants.

TABLE 2.

Type I. Evergreen. *Picea excelsa* dominant. Bickleigh, Devon. 5.9.29. Sun clear, cloudless sky. Very light haze.

(Soil moist throughout the wood.)

Base A. Towards the bottom of wood. Site and Vegetation.	G.M.T.	β	Illumination in metre candles. V_s	V_0	Percentages. $\frac{V_s}{V_0}\beta = \delta$
1. 4·5 m. in wood from edge of lower bank; no growth at all excepting 2 seedlings of *Hedera helix*, each with two leaves.	1.42	2·4	270	56,500	1·1
2. 4·5 m. in wood from edge of lower bank at a spot where a tree of Picea had been recently felled; no growth.	1.44	2·4	600	57,000	2·5
3. 0·5 m. from edge of lower bank; *Scilla nutans*, 2, and a few small plants of *Oxalis acetosella*.	1.48	2·4	2,650	58,000	10·9
4. 1 m. away from site 3 (to the right and horizontally).	1.49	2·4	2,520	58,000	10·3
5. Extreme edge of lower bank of wood. Scilla, 3, a few plants of Oxalis and one small *Conopodium denudatum*.	1.52	2·5	4,410	59,000	17·8
6. 2–3 m. within lower part of wood; small moss patch and 1 seedling of Hedera.	1.55	2·5	1,740	59,000	7·8
7. About 6 m. in from bottom of wood; a seedling each of Quercus and Hedera.	1.58	2·5	540	58,000	2·3
8. 10 m. in from bottom of wood; small clearing of 3 m. sq. Oxalis, 3, 1 seedling Hedera, 6 small *Stellaria media*, young plant of *Lychnis dioica*.	2.1	2·5	1,060	59,200	4·5
9. 15 m. inside bottom part of wood, small moss patch, several seedlings of Hedera, small Lychnis and *Viola canina* without flower.	2.6	2·5	530	60,000	2·2
10. 20 m. within lower part of wood; bare patch without growth for 6 m. square.	2.15	2·5	400	60,600	1·6
11. 21 m. in at narrow track about 25 cm. wide; small plants of Hedera.	2.17	2·5	420	60,600	1·7
Base B. About middle of wood.					
1. 21 m. in from bottom of wood at level track 25 cm. wide.	2.52	2·2	395	56,000	1·6

2. Opposite side of track at base of small bank about 1 m. high; small plants of Oxalis, several small plants of Hedera and one small Aspidium and Blechnum.	2.55 2.57	2·2 2·2	386 396	56,500 54,000	1·5 1·7
3. Some distance above site 2; three very fine plants of Aspidium (leaves 1 m. long). Very sparse carpet of Hedera and larger leaved Oxalis than at site 2. Four small trails of *Lonicera periclymenum*, and one small trail of *Rubus fructicosus*.	3.0	2·2	631	54,000	2·6
4. At base of slender tree of *Fraxinus excelsior* about 12 m. high; small Fraxinus 2 m. high, 1 m. away, tangle of straggling Rubus, one Aspidium and some Oxalis.	3.5	2·2	950	53,000	1·8*
5. 2 m. above 3, level clearing about 9 × 3 m.; moss mixed with Oxalis, one *Digitalis purpurea* and *Primula vulgaris*, 1 seedling Fraxinus with 2 foliage leaves, and straggling Rubus.	3.9	2·2	710	52,500	3·0
6. 12 m. above site 5; Rubus with poor fruit, one Aspidium (leaves 2 feet long) 1 large Blechnum, shrub of *Corylus avellana* 1 m. high, young Fraxinus 1 m. high and a little Oxalis.	3.17	1·9	899	52,500	1·7*
Base C. Well towards the top of the wood.					
1. About 12 m. from the top of the wood; young Quercus 1 m. high, tall Rubus with ripe fruit, small Fraxinus and *Acer pseudo-platanus* seedling, one Digitalis in flower, one large Carduum (sp. ?), one Aspidium and some *Hylocomium splendens*.	4.21	1·6	631	29,000	3·5
2. About 9 m. from top; shrub of Corylus 3 m. high, small trails of Lonicera, *Lychnis dioica* in flower, tall Rubus trails and a little Oxalis.	4.24	1·6	663	30,000	3·6
3. About 6 m. from top; Lychnis in flower, small frond of Pteris, Hedera climbing up trees of Picea, trails of Lonicera, small plant of *Nepeta glechoma* and *Tamus communis*.	4.27	1·5	946	29,500	4·8
4. About 3 m. from top of wood; Corylus 3 m. high, Scilla with ripe fruit, saplings of Acer and Fraxinus 1·5 m. high, one plant of *Circaea lutetiana*, small Tamus, Nepeta and one *Geranium robertianum*.	4.28	1·5	631	29,500	3·20
5. About 2 m. from hedge at top of wood; dense tangled undergrowth, tall *Dactylis glomerata* and other grasses, *Rumex obtusifolius*, *Galium aparine*, Tamus, *Rosa canina*, *Geum urbanum* and *Urtica dioica* in flower.	4.35 4.36	1·5 1·5	1,730 2,210	28,600 27,600	9·20 8·1*

* Values of $\frac{V_s}{V_0}$, sun fleck on photometer window.

Type II.

Deciduous Gymnosperm.

Dominant—*Larix europaea.*

The wood studied is a triangular plantation at Shaugh, Devon, situated on a slight slope facing east. It is bounded at its upper limit by a railway line, the lower part ending in a zone of Pteris, which forms the top of a hedge-bank skirting a road. With the exception of one or two old trees of *Quercus robur,* Larix is in pure stand. Most of the trees are from 8–10 m. high, and are planted about 2 m. apart.

The open base was in a field on the opposite side of the railway cutting.

Base A was within the upper and steepest part of the wood.

Base B was a position near the bottom and more level portion. The soil was damp at all the sites studied.

Table 3 supplies the data of the flora and daylight factors for the selected sites.

The variety of growth under the larch trees is partly accounted for by the slope of the ground, which, facing east, receives early morning sun. The average daylight factor within the wood is about 16 per cent., grasses growing fairly well in most parts, except in the lower and level part, where there is a zone of tall thickly growing Pteris about 2 m. wide, under which only Hedera and Oxalis are found, δ being reduced to 3 or 4. Under the heavy shade of an old tree of Quercus with a broad crown, $\delta = 7$; under the oak there is no grass, its place being taken by a carpet of Hedera. Lonicera also is found at a low value of δ. Rubus appears frequently and at varying light intensities, bearing ripe fruit at $\delta = 16$ and over. *Galium aparine* was found where $\delta = 16{\cdot}6$, and *G. mollugo* was abundant at $\delta = 21{\cdot}4$.

TABLE 3.

Type II. Larch Wood (*Larix europaea*), at Shaugh, Devon. 9.9.29. (Soil moist for all sites.) Sun out and few clouds low down towards N.E. From 12.9 onwards a few long cloud fingers S.W. to N.W.

Base A.	Near railway towards top of slope. Site and Vegetation.	G.M.T.	Illumination in metre candles. β	V_s	V_0	Percentages. $\frac{V_s}{V_0}\ \beta = \delta$
1.	Immediately outside the upper limit of the plantation. Bank of tall mixed grasses, with a little Pteris and one or two trails of Lonicera from the wood.	11.42	2·9	18,800	60,500	88·0
2.	Just within the upper level of the wood 1 m. down from site 1. The ground here is shaded by the tall grasses of 1. Pteris 1 m. high with thin trails of Lonicera climbing up the fronds, Rubus with ripe fruit, mixed grasses.	11.48	2·9	3,800	63,500	17·2
3.	6 m. inside wood and in a small clearing; 5 plants *Solidago virgaurea*, low trails of Rubus, 1 Digitalis in flower, 1 plant of *Stachys officinalis* in flower, carpet of low mixed grasses and one or two pieces of Hedera.	11.54	2·9	3,160	64,500	14·2
4.	Some distance inside the wood, but under the shade cast by the low spreading crown of an old *Quercus robur*; several plants of Stachys, 3 of Pteris, no grass, complete but loose carpet of Hedera.	11.57	3·0	1,610	64,500	7·5
5.	About 3 m. further down the wood, and just outside the shade of Quercus (site 4); short Pteris (0·5 m. high) dominant, 2 tall plants Solidago, thriving Rubus in ripe fruit, some *Galium verum*, *Teucrium scorodonia*, some grass mixed with moss.	12.9	3·1	3,840	69,500	16·6*
6.	About 6 m. below 5; just outside a zone of Pteris 1 m. high, Teucrium, low trails of Rubus, very little grass, sparse carpet of Hedera and Oxalis.	12.19	3·1	7,990	70,500	11·3†
7.	Amongst the Pteris zone of site 6 (1 m. in); Hedera and Oxalis growing on ground under the fronds.	12.22	3·1	975	72,000	4·2

TABLE 3—*continued.*

Base A.	Site and Vegetation.	G.M.T.	β	Illumination in metre candles. V_s	V_0	Percentages. $\frac{V_s}{V_0}\beta = \delta$
	Near railway towards top of slope.					
8.	Same level as 7 but 2–3 m. away (horizontally); very straggling Rubus without fruit, tangle of stunted Lonicera, a few pieces of Teucrium, carpet of Hedera and Oxalis.	12.26	2·8	770	68,000	3·2
Base B.	Towards lower part of wood near road.					
1.	2–3 m. to left of site 8, Base A; still amongst the Pteris zone. ...	2.20	2·7	1,670	60,500	7·6
2.	3 m. inside wood from lower boundary, and just outside the Pteris zone of 1; *Bromus asper*, Pteris, one Digitalis, carpet of Oxalis and Hedera.	2.22	2·7	2,210	56,000	10·8
3.	1 m. in from extreme lower bank of plantation; *Galium mollugo*, *Veronica germanica*, Rubus; Hedera climbing up the tree trunks, *Rumex acetosa* and low mixed grasses.	2.43	2·0	6,210	58,000	21·4
4.	Extreme edge of lower bank.	2.49	1·5	13,800	44,500	46·5
5.	Just within a zone of Pteris, Hedera and Oxalis forming a carpet. ...	3.7	1·6	2,770	51,000	8·6
6.	5 m. inside wood from road; group of tall plants of *Teucrium scorodonia*, with straggling Hedera between them.	3.11	1·5	4,550	46,300	14·8
7.	5 m. in from road but 2 m. to right from site 6; plants shaded by a patch of *T. scorodonia* to left; *Solidago virgaurea*, thin trails of Lonicera, shorter plants of Teucrium, Rubus and low mixed grasses.	3.14	1·3	2,510	42,500	7·7

* $\frac{V_s}{V_0} = 5{\cdot}5$, small sun fleck on photometer.

† $\frac{V_s}{V_0}$, sun on photometer.

Type III.

Mixed Deciduous.

Dominants—*Quercus robur* var. *sessiliflora* in upper parts giving way to *Larix europaea* lower down.

This area was about 3 or 4 kilometres along the railway line from the larch plantation at Shaugh, and, like it, slopes eastwards, and is bounded by the railway line at the top and a road at the base. For the first 15 m. from the top it consists of *Quercus robur* var. *sessiliflora*. Below this, and divided from it by a path about 30 cm. wide, *Larix europaea* is dominant, with Quercus subdominant, the trees being closer together in this part.

The open base was the wall of a railway bridge just outside the wood. Base A was within the upper zone, with Quercus dominant, and base B lower down and within the larch zone.

Table 4 furnishes data for this wood.

Its comparatively low value for the daylight factor is reflected in the flora. Towards the top of the wood quite a variety of herbaceous plants are found. (Sites 6 and 7, base A), several of those are found only at the outskirts, e.g., Galium, Rumex, and Nepeta. Rubus may be said to be the dominant undergrowth in the upper portion, with Quercus as the dominant tree, but further down the slope, with gradual introduction and increase of *Larix europaea*, this is replaced by Hedera. The upper portions permitted of good growth of seedlings of Quercus and Acer, but these become very poorly developed under the larch.

Type IV.

Evergreen Angiosperm.

Dominant—*Quercus ilex.*

The last type of woodland studied was composed mainly of trees of *Quercus ilex*. It is situated on the road to Antony, S.E. Cornwall, on level ground running from north to south, narrowing considerably towards the southern end, where deciduous trees replace the Quercus. A few trees of *Acer pseudo-platanus* occur near all the margins of the wood. The open base was a bank on the road. Base A was in the wider (north) end. Base B was towards the middle and near a small footpath which runs N.–S. through the wood, and base C well towards

TABLE 4.

Type III. Oak-Larch Wood. Near Bickleigh, Devon. 6.9.29. (Soil damp in all the sites.) Sun clear, light haze high up; wind N.

Base A. Site and Vegetation.	G M.T.	Illumination in metre candles. β	V_s	V_0	$\frac{V_s}{V_0} \beta$
Near railway. *Quercus robur* var. *sessiliflora* dominant.					
1. At level of a small track half way down the slope of the wood; tangle of Rubus about 0·5 m. high bearing ripe fruit, a few straggling plants of Hedera and some *Lychnis dioica*.	11.48	2·0	2,520	65,100	7·8
2. 2 m. above 1; Rubus with ripe fruit and flower, plant of *Teucrium scorodonia*, small *Nepeta glechoma*.	11.56	2·0	17,300	66,500	25·7*
3. 3 m. above site 2 and 12 m. from the top of wood, at a small clearing; Rubus with fruit and flower, small white vetch (species unknown) climbing up Rubus, Teucrium about 0·5 m. high, Scilla with ripe capsules, one or two pieces of straggling Hedera.	12.3	2·0	3,150	67,500	9·3
4. 2 m. higher up slope between two trees of Quercus 12 m. high; tangle of Rubus, a seedling of Quercus with three foliage leaves, 2 small seedlings of *Acer pseudo-platanus*, *S. nutans* with ripe capsules, 2 flowering Digitalis.	12.9	2·0	12,200	69,000	17·7*
5. 9 m. from top of wood; low Rubus in fruit, Teucrium, *Viola canina*, seedling Acer.	12.20	2·0	14,700	70,500	—
6. 3 m. from top of wood; small open patch 5 × 5 m.: *Lychnis dioica*, *Geranium robertianum*, very long trails of Rubus, young Acer 40 cm. high, Scilla with fruit and *Linaria vulgaris*.	12.25	2·0	13,300	71,500	39·2
7. Just below first tree at top of wood; straggling Rubus, one Digitalis, Hedera climbing up tree trunks, *Geranium robertianum*, 1 *Rumex obtusifolius* about 1 m. high, Nepeta, 2 seedling Acer, *Galium aparine* climbing up tree.	12.28	1·9	4,200	74,000	10·8
Base B. *Larix europaea* now dominant.					
1. About 3 m. below site 1, Base A, i.e. about 18 m. from top of wood; Rubus with small green fruit, Teucrium 0·3 m., a little Hedera, a few fronds of Pteris and 1 Aspidium. This site is just below the first row of trees of Larix.	2.2	1·8	1,960	58,000	6·1
2. 5 m. below site 1; low straggling Rubus, sparse carpet of Hedera, a little Pteris.	2.21	1·6	2,040	57,000	5·7
3. 6 m. within the zone with Larix dominant; low shrub of Corylus (1 m. high), straggling Rubus with red fruit, sparse carpet of Hedera with one or two fronds of Pteris, unhealthy seedling of Acer.	2.26	1·6	2,080	57,000	5·9
4. 11 m. within the Larix zone; straggling Hedera and stunted Rubus. ...	2.36	1·59	850	55,000	2·5

* Values of $\frac{V_s}{V_0}$, sun flecks on photometer.

the south end. Table 5 gives the daylight factors for the plants observed at the various sites.

With $\delta = 1$ and 2·5, *Hedera helix* is dominant, forming a close unbroken carpet. As δ rises the ivy becomes more open, being absent with $\delta = 11$–18, but appearing on the northern side of some trees where the value for δ is reduced to 2·8.

The appearance and gradual increase of *Urtica dioica* is interesting. In the spruce wood at Bickleigh, Urtica appeared at the upper open region in a fairly healthy state with $\delta = 9{\cdot}2$. In the holm oak wood it first appears in a stunted yellowish condition with $\delta = 3{\cdot}7$, increasing in height and colour with rise in the daylight factor, being over 1 m. tall, with flowers, when $\delta = 19$, and competing with tall grasses and other herbaceous plants.

Galium aparine appears in a stunted condition with $\delta = 11$–19.

Species of Carduus were found with such values of δ, whilst a young plant of *Arctium lappa* was growing in the pathway with $\delta = 11$.

Under an *Ilex aquifolium* δ was 0·6, and there was no growth. This was the minimum value of δ recorded in this paper, Table 5 A 10.

General Discussion.

From measurements of the daylight factor in selected shaded sites, it is possible to make a comparison of the intensities of the illumination in four different types of woodlands, and a study of the floras found at the shaded sites makes it possible to attempt to correlate light intensity with plant distribution.

With *Picea excelsa* dominant, $\delta = 1{\cdot}1$, and stunted plants of Hedera and Oxalis formed the only undergrowth, the ground being covered with dry dead leaves of spruce. At the top of this wood, where the presence of a few deciduous trees and their lesser height raised the value of δ to 9·2, a fair variety of herbaceous plants constituted the undergrowth. These included low bushes of Corylus, tall grasses, *Rumex obtusifolius, Urtica dioica, Tamus communis, Lychnis dioica,* etc. (Table 2).

A wood with *Larix europaea* dominant had an average daylight factor of 15. Mixed grasses appeared in the greater part of the wood, with *Rubus fruticosus* represented at most sites. Pteris was dominant with δ about 11, the daylight factor being reduced to 4 underneath the fronds.

In a steeply sloping wood, with *Quercus robur* dominant at its upper limits, δ may be taken at an average value of 9. Rubus appeared at most of the sites, generally bearing fruit. Closely planted and taller *Larix europaea* lowered δ to 6·1–2·5 towards the bottom of the slope. There was no grass throughout the wood.

A plantation of *Quercus ilex,* with daylight factor 1–4, had *Hedera helix* the dominant undergrowth. A rise in δ to 11, owing to admixture of deciduous trees at the southern boundaries, caused Hedera to be supplanted by grasses and a variety of herbaceous plants, these being very tall and healthy with $\delta = 18$–19.

TABLE 5.

Type IV. Evergreen. *Quercus ilex* dominant, near Antony, S.E. Cornwall. 12.9.29. Sun clear, sky blue, light haze, very small clouds to N. up to 10.30 ; then light clouds near or over sun, reducing β to 2 or less after 11.25.

(Soil drier than preceding types but still moist.)

Base A.	At north end, about 12 m. in from road. Site and Vegetation.	G.M.T.	β	Illumination in metre candles. In Wood. V_s	In Open. V_0	$\frac{V_s}{V_0}\beta$
1.	About 11 m. in from road, typical portion of wood. At base of tall tree of *Quercus ilex* near a narrow path 30 cm. wide ; close carpet of *Hedera helix* 15 cm. high, one seedling *Acer pseudo-platanus* with 4 foliage leaves and 1 seedling Fraxinus.	10.3	2·8	570	52,500	1·1*
2.	Base of another tree. Pure carpet of Hedera 15 cm. high.	10.4	2·9	220	53,500	1·2
3.	Between sites 1 and 2, but nearer road ; very fine plant of *Scolopendrium vulgare* (leaves 40 × 6 cm.), 2 seedlings of Acer, 1 seedling Fraxinus, 3 small trails of Lonicera, carpet of Hedera.	10.7	3·0	420	54,500	2·3
4.	Still nearer the road ; carpet of Hedera a little taller and not so close as 2, small trails of Rubus, and 3 small pieces of *Ligustrum vulgare*.	10.12	3·0	350	57,200	1 8
5.	14 m. in from road ; open patch surrounded by old trees of *Q. ilex*, 2 fine plants of Aspidium, 1 Scolopendrium, *Geranium robertianum* (very fine plant), 1 seedling Acer, 2 pieces of Ligustrum, Hedera.	10.19 10.27	3·1 3·1	610 820	54,000 60,000	3·5 1·4*
6.	2–3 m. from 5, near stump of old Crataegus ; low trails of Rubus with green fruit, *G. robertianum*, 4 plants *Viola canina* in fruit, carpet of Hedera.	10.34	2·1	550	60,500	2·8
7.	3 m. from site 5 ; Rubus with green fruit, *G. robertianum*, *Veronica germanica*, carpet of Hedera more open.	10.35 10.36	3·1 3·1	7,400 550	60,500 61,500	12·4* 2·7
8.	At base of tall tree, *Quercus robur* near a footpath 1 m. wide and 15 m. in from road ; thick carpet of Hedera, very fine *G. robertianum*, few short trails of Rubus and 4 straggling plants of *Urtica dioica*.	10.39	2·6	500	64,000	2·5
9.	Opposite side of path in 8, under close canopy of tall *Q. ilex* ; low but very long trails of Rubus, one *G. robertianum* with rosette of leaves 30 cm. long and bearing fruit, fairly open carpet of Hedera.	10.44	2·8	770	56,000	3·8
10.	Under a bush of *Ilex aquifolium* with leaves commencing 45 cm. from ground, absolutely no growth under bush, but low close carpet of *H. helix* near.	10.47	2·9	140	70,000	0·6

Base B.	About middle of wood.				
1.	About 18 m. in from road between 2 tall trees of *Acer pseudo-platanus* and *Q. ilex*; low trails of Rubus with green fruit, 6 plants of *Circaea lutetiana*, open carpet of Hedera.	11.22	2·5	,230	57,500	3·9*
2.	1·5 m. to left of site 1; *Circaea lutetiana*, 3 stunted *Urtica dioica*, 1 *G. robertianum*, straggling Rubus and carpet of Hedera.	11.24	2·5	950	64,500	3·7
3.	2 m. to left of site 2; small patch of tall thin Urtica 60 cm. with flowers, 2 large plants of Scolopendrium, Rubus with green fruit and carpet of Hedera.	11.25	2·0	600	76,500	1·5
4.	Near site 3 in sun.	11.28	2·4	14,100	64,500	21·8*
5.	By patch of tall unhealthy Urtica, carpet of Hedera.	11.30	2·1	630	81,500	1·6
		11.32	1·8	750	69,500	1·9
6.	6 m. away under tall trees of Acer and *Q. ilex*; open carpet of Hedera and *Sanicula europaea* in fruit.	11.34	1·9	1,630	76,500	4·1
Base C.	Well towards the southern end of wood.					
1.	14 m. in from S. end, near pathway running through wood; mixed grasses, tall Rubus with ripe fruit, tall Urtica (1·2 m.) with flowers, *Rumex obtusifolius* (1 m.), *Plantago major*, young *Arctium lappa* (in pathway), *Nepeta glechoma*, no Hedera.	11.48	2·0	4,400	80,000	11·0
2.	12 m. from S. end of wood; thistle in fruit, *Circaea lutetiana*, *Plantago major*, very tall Urtica, mixed grasses, no Hedera.	11.50	2·0	7,700	81,000	19·0
3.	11 m. from S. end of wood; Rubus with ripe fruit, short *Galium aparine*, tall Urtica, tall mixed grasses.	11.53	2·0	7,450	80,500	18·6
4.	6 m. from S. end of wood; at base of tall *Quercus robur* (on N. side), small branches of Hedera, *Geum urbanum*, no grass.	12.1	2·0	900	80,500	2·8

* Values of $\frac{V_s}{V_0}$, sun flecks on photometer.

From data supplied by tables of the flora for sites within the four woods, it would appear that Hedera flourishes best with $\delta = 1{\cdot}5$–7, usually being dominant with the daylight factor between 1·1 and 3·4, and seldom appearing beyond $\delta = 16$. It is of interest to notice in connection with this the occurrence of Hedera in the immediate shade afforded by a large oak tree on its N. side (Table 5 C 4), where δ was reduced to 2·8. In the surrounding sites, where $\delta = 19$, Hedera was absent. Oxalis was frequently associated with Hedera when the daylight factor was 7 and under.

Very fine plants of *Scolopendrium vulgare* were observed in heavily shaded sites in two of the woods studied, where $\delta = 1{\cdot}5$, 2·3, 3·5, and an exceptionally fine Aspidium appeared with $\delta = 3{\cdot}5$.

Rubus fructicosus was observed with a very wide range, with δ varying from 1·8–32·2. With the daylight factor below 4·5, the trails were usually very short, straggling and low, in an unhealthy condition. Above 7 the trails were longer, thicker and taller, becoming a dense tangle, difficult to negotiate.

Pteris occurred as a dominant, with δ 11–16 in the larch wood at Shaugh, few other plants being associated with it because of the heavy shade cast by the fronds, but Hedera and Oxalis frequently occur under the Pteris.

In the sites observed grasses appeared only when the general value of the daylight factor was above 9, being very tall and vigorous, tending to choke other herbaceous growth in two sites with $\delta = 11{\cdot}6$ and 19. Being near the edge of the wood, the maximum illumination would naturally exceed these values.

In the holm oak wood an interesting progression in the growth of *Urtica dioica* was observed as the daylight factor rose from 1·5–19·6. In the first site where Urtica occurred, three plants about 20–30 cm. high appeared, bearing yellowish leaves and having a general stunted condition. A larger and taller, although still unhealthy, group of Urtica was found with $\delta = 3{\cdot}7$. With the daylight factor 18 and 19, the plants were quite 1·2–1·5 m. high, very healthy, competing and in some places gaining dominance over tall crowded grasses.

It may be observed that although seedlings of *Acer pseudo-platanus*, *Q. robur*, and Fraxinus are recorded for several sites which have low values of δ (e.g., 1·1, 2·3, 3·5), these were all in the first year of growth, and it is possible that these are able to grow here partly by virtue of their food reserves during this time, since very few seedlings of more advanced stages were found.

From these selected examples it may be seen, that although the nature of the woods may differ widely, being evergreen or deciduous, certain plants growing in them, such as grasses, Hedera, Rubus, Scolopendrium, Urtica, etc., do, by their appearance and condition of growth, give some idea of the value of the light intensity for the site in which they are found.

Summary.

1. A portable photo-electric outfit, previously described, has been found serviceable for determining daylight factors in woods. The assembly for use in shaded sites weighs 11·5 kg. (25 lbs. 7 oz.), case included, and might possibly

be reduced by 2–3 kg. That for use in the open weighs 6·2 kg. (13 lbs. 12 oz.), with case, and further appreciable reduction is unlikely.

2. Under shade from *Picea excelsa*, pure stand, the daylight factor, δ, was reduced to 1–2 per cent. There was little or no growth save occasional seedlings of *Hedera helix*, with a little *Oxalis acetosella* becoming more frequent with δ = 3–4. With δ 9 there was a tangled undergrowth of *Rubus fructicosus* and saplings of *Corylus avellana, Fraxinus excelsior*, and *Acer pseudo-platanus*.

3. Under shade from a narrow wood of *Larix europaea*, nearly pure stand, the value of δ was about 15 per cent.; there was an undergrowth of Rubus in fruit, a belt of *Pteris aquilinum*, and a good woodland flora.

4. In a mixed *Quercus robur* and Larix wood, the upper (oak) portion had δ about 10, with much tangled undergrowth. In the lower (larch) portion δ fell to 2·5 to 6 per cent., and *Rubus fructicosus* became greatly reduced in size and quantity. The ground had a sparse carpet of Hedera. The three woods mentioned were on steep slopes, positions which themselves tend to reduce illumination.

5. A wood of *Quercus ilex* on level ground gave values of δ 1–2 or 3 per cent.; in many sites there were pure carpets of Hedera. Under *Q. robur* δ was found to be 2·8 per cent. Hedera was replaced by grasses with δ = 19. The deepest shade found was under *Ilex aquifolium*, δ = 0·6 per cent.; nothing grew there.

As acknowledged in Part II, the major part of the apparatus was purchased out of a payment from the Government Grant Committee of the Royal Society, and the universal shunt was lent by the Marine Biological Association, Plymouth.

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No. 46.

THE DISTRIBUTION OF PASTURE PLANTS IN RELATION TO SOIL ACIDITY AND OTHER FACTORS.

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In a former paper (1922) it was shown that the hydrogen ion concentration of the soil was a factor of much importance in regulating the distribution of plants. It seemed desirable, in a continuation of the work, to attempt to elucidate the factors affecting the grasses and leguminous plants which constitute the bulk of those found in pastures.

The work may be roughly grouped as follows:—

(*a*) Records obtained, mostly in Devon, in the course of advisory work on farms.

(*b*) A more detailed examination of twenty-two sites in permanent pastures at Seale-Hayne Agricultural College, Devon.

(*c*) An examination of fifty-one sites, of which forty-five were permanent pasture at the Boghall Experimental Farm, of the Edinburgh and East of Scotland College of Agriculture, in the Pentland Hills.

(*d*) Persistence trials over a period of six years in garden plots at Antony, near Torpoint, in Cornwall.

Much of the area of the British Isles consists of hill and other poor pasture land. In seeking to improve this it should be borne in mind that any attempt to transform it into really good pasture must of necessity be of high initial cost, with probably a considerable cost of maintenance added on. Only rarely, therefore, can it be an economically sound proposition. If, however, a knowledge be gained of the soil conditions under which our native grasses and leguminous plants thrive and persist permanently in any site it seems to be quite feasible to modify soil and grazing conditions in certain localities, at no very great

expense, so as to render the ground capable of supporting a superior grouping of pasture plants. An essential requirement of pasture land is the ability to maintain its supply of nitrogenous substances, otherwise the addition of nitrogenous fertilizers becomes a costly necessity. Since leguminous plants, mainly the clovers, fix nitrogen in their root nodules, this requirement is reduced to the ability to support the growth of clovers, &c. Of these, wild white clover, *Trifolium repens* L., is the mainstay of our more acid pasture lands, as mentioned in our provisional report (1923) and shown by the hydrogen ion concentration measurements given below.

Analyses showed that such upland pastures are very poor in soluble phosphate, and, as is well known, practical results in many places have demonstrated the value of basic slag or superphosphate in improving the pasture (see, for example, Smith, 1918 and 1923). The phosphate encourages the clover, which brings more nitrogen into circulation. The low soluble phosphate content of acid soils is due to a combination of factors: firstly, the poorness of the rocks or sediments giving rise to them; secondly, the removal of soluble phosphate by heavy rainfall, which by leaching out bases gives rise to the acidity; and, thirdly, the fact that such acid soils are usually richer in soluble salts of iron. Both ferrous and ferric phosphates begin to be precipitated in markedly acid solutions, at about *pH* 3, consequently soils sufficiently acid to have much iron in solution can have but little soluble phosphate. The addition of a phosphatic manure, however, will precipitate nearly all the iron, leaving phosphate in excess available. It is more economical as regards phosphate to lime first.

Since this study was undertaken a number of papers have appeared dealing with the relation of soil reaction to agricultural and other plants. A very few of these are cited in the list of references, which is a continuation of that in the 1922 paper. For economy of space no attempt has been made to discuss them here. The extensive bibliography, 759 titles, given by Mevius (1927) may be consulted. Information concerning the grasses has been given by Armstrong (1921). Stapledon and Hanley (1927), too, have summarized recent work upon the improvement of grass land.

The composition of pastures varies from field to field. Data on such variation in Devon have recently been provided (Fenton, 1927); the constituents may also be largely affected by the character and amount of the grazing to which the pasture is subjected (Fenton, 1926). The factors regulating the delicate balance between the various pasture grasses are not, however, readily evaluated. The moisture-holding qualities of the soil, the angle and direction of slope, and the exposure to wind are all of much importance, in addition to the more readily measurable chemical characteristics.

It is hard to ascertain any definite limiting factor for grasses save in extreme cases. One does not find *Bromus asper*, for example, in an open field, since it is crowded out by other grasses, but it occurs in shaded sites along

with them, and penetrates further into the shade (1926). A few grasses only, such as *Festuca ovina* var. *rubra,* can stand being submerged by brackish water, approaching the salinity of sea water, at spring tides. Again, the widely distributed *Agropyrum repens* is generally found in arable fields, by the road side and in waste places generally. It gets a good chance, undisturbed, with cereals, but with root crops the constant cultivation eradicates it. Heavy, or even moderate, grazing it cannot stand. It may be noticed that it did not figure as a grass sufficiently important to warrant mention in any of the pastures listed in Table 2. Only once was it observed to be prevalent in a grass field. In this case it appears probable that the field had not been properly cleaned before the seeds mixture was sown.

It is almost impossible to give a numerical value to the frequency with which a grass is found within a given area, because many have creeping stems rooting at intervals. Similarly, it is not feasible to measure the area covered by individual plants. The weight of foliage that can be grazed would be a desirable index, but even when the green parts are cut off, sorted, and weighed there may be considerable differences according to the season at which this is done. Clippings were, however, taken from turf samples from a field at South Molton, Devon, in June, 1923; these were sorted and weighed. The samples were from nine areas on one side of a field, Nos. 1 and 7 being corners, also from the other two corners and centre, making twelve in all. Agrostis predominated in Nos. 1, 7, 8, 9, and centre, Anthoxanthum in Nos. 2 and 3, *Holcus lanatus* in Nos. 4, 5, 12, and 6, bracketed with *Cynosurus cristatus* in 6, the last-named alone predominating in No. 11. This method gave the average composition of the pasture as Agrostis 35 per cent., Holcus 20 per cent., Anthoxanthum 13 per cent., Cynosurus 12 per cent., *Bromus mollis* 4 per cent., *Festuca ovina* 4 per cent., *Trifolium repens* 2 per cent., *T. pratense* 0·8 per cent., Musci sp. 2 per cent., *Lolium perenne* 2 per cent., Poa sp. 0·7 per cent.; weeds, Ranunculus sp., *Bellis perennis,* Hieracium sp., *Rumex acetosella,* Cerastium sp., together 1·2 per cent., total 96 per cent. The soil in the centre was at *pH* 5·6, determined by the quinhydrone electrode; the other sites were within about plus or minus 0·2 units as determined colorimetrically. The method gives a fair idea of the composition of the pasture, though the total amount of herbage analysed, 28 grams. fresh weight, was too small. The method is, however, even with these quantities, very laborious.

Another example, of a very different type, may be given. This was from an area of carboniferous limestone at Newton St. Cyres, near Exeter. Its reaction was *pH* 7·3, and its phosphate, as P_2O_5, in water extract (1 soil to 5 water) was 15 parts per million calculated on air-dry soil as against under 1 p.p.m. for various acid hill pastures. Analysis gave *Festuca ovina* 37 per cent., *Bromus mollis* 12 per cent., *Lolium perenne* 11 per cent., *Agrostis palustris* 7 per cent., *Poa trivialis* 7 per cent., Musci spp. 20 per cent., *Trifolium repens* 2 per cent., weeds and loss 4 per cent.

As a general rule in the present work a visual estimate only was made, the grasses listed being the most important constituents. Special care was, however, taken to mention the presence of leguminous plants. In the S. Molton field examined *Trifolium repens* was found in 10 out of the 12 sites; two of these also had *T. pratense.*

Ranges of pasture grasses.

Table 1 contains records of the predominant grasses found in the pastures, including some waste ground, examined previous to September, 1923, when we communicated preliminary results. The soils ranged from *pH* 5·0–8·0, and within this range no very marked limitation of the grasses by soil acidity could be made out; moreover, the number of samples was not very large, though the absence of a species goes unrecorded, and may be quite as significant as its presence. Table 2 is more conclusive. It records the species which were found as natives at the Seale-Hayne Agricultural College or at the Boghall Farm in permanent pastures.

TABLE 1.

Based on examination of over fifty pastures, *pH* 5–*pH* 8.

Grasses.	No. of sites.	*pH* range.
Agropyrum repens, Beauv. Couch grass	4	5·5–7·2
Agrostis palustris, Huds. Bent grass	20	5·6–8·0
Arrhenatherum avenaceum, Beauv. Tall oat grass ...	1	5·5
Avena flavescens, L. Yellow oat grass	3	6·2–7·2
Bromus mollis, L. Soft brome grass	1	7·5
Cynosurus cristatus, L. Crested dog's tail	10	5·6–7·2
Dactylis glomerata, L. Cock's foot	5	5·8–7·8
Festuca elatior, L. sub-sp. *pratensis,* Hackel. Meadow fescue	1	6·9
Festuca ovina, L. Sheep's fescue	7	5·0–7·8
Holcus lanatus, L. Yorkshire fog	2	6·4–6·6
Holcus mollis, L. Creeping soft grass	4	5·4–7·2
Hordeum murinum, L. Wall barley	2	7·8
Lolium italicum, Braun. Italian rye grass	1	5·8
Lolium perenne, L. Perennial rye grass	14	5·8–7·8
Phleum pratense, L. Timothy or cat's tail	2	6·9–7·2
Poa annua, L. Annual meadow grass	7	5·8–7·8
Poa pratensis, L. Smooth-stalked meadow grass ...	3	6·0–7·8
Poa trivialis, L. Rough-stalked meadow grass ...	1	7·8

TABLE 2.

Distribution of grasses in relation to soil reaction. *pH* values given as 7·5, 7·0 . . . 3·5 denote the ranges 8·0–7·5, 7·5–7·0 . . . 4·0–3·5.

	Seale-Hayne.					Boghall Farm.						
pH values	7·5	7·0	6·5	6·0	5·5	6·5	6·0	5·5	5·0	4·5	4·0	3·5
No. of sites	3	11	3	3*	2*	2	4	3	11	13	13	5
Agrostis palustris Huds. ...	3	3	2	1	2	1	3	1	8	8	8	1
Aira caespitosa	—	—	—	—	—	1	1	—	—	—	—	—
A. flexuosa	—	—	—	—	—	—	—	—	1	1	2	3
A. praecox	—	—	—	—	—	—	—	—	—	—	1	—
Alopecurus pratensis	—	—	—	—	—	—	—	1†	—	—	—	—
Anthoxanthum odoratum ...	—	2‡	—	—	—	—	3	—	7	2	3	—
Arrhenatherum avenaceum ...	—	—	1	1	—	—	—	—	—	—	—	—
Briza media	—	3	—	—	—	—	2	—	—	—	—	—
Cynosurus cristatus	—	1	2	3	2	—	2	—	—	—	—	—
Dactylis glomerata	—	2	—	—	—	—	—	—	—	1§	—	—
Festuca elatior sub-sp. *pratensis* Hackel.	—	2	—	1	—	—	—	—	—	—	—	—
F. ovina	—	—	—	—	—	1	3	1	7‖	7‖	6‖	4‖
F. ovina var. *duriuscula* Koch ...	—	—	—	—	—	—	1	—	—	—	—	—
Holcus lanatus	—	5¶	—	—	—	—	1	—	2	1	—	—
H. mollis	—	—	—	—	—	—	—	—	—	2**	2**	—
Lolium perenne	—	6	—	3	1	—	—	—	—	1§	—	—
Nardus stricta	—	—	—	—	—	—	1	1	3	5	5	4
Phleum pratense	—	—	—	—	—	—	—	1†	1†	—	—	—
Poa annua	—	—	—	—	—	—	—	—	1	—	—	—
P. trivialis	—	—	—	—	—	1	—	—	—	—	—	—
No. of sites open to grazing ...	3	11	3	3	2	2	4	3	11	9	11	5
No. of sites grazed or slightly grazed.	3	11	3	3	2	2	3	3	8	1	1	0
Slightly grazed only ...	0	0	0	0	0	0	1	1	2	1	1	0

Soils at *pH* 5·0–4·5 were somewhat peaty or matted; those at 4·5–4·0 were largely peaty; those at 4·0–3·5 were peaty.

* Moss abundant at *pH* 5·8 and 6·2, one site each. † Not growing well.

‡ Dominant in two sites. § A few plants only in enclosed corner, stunted.

‖ Recorded as traces only in two of the listed sites. ¶ Dominant in four sites.

** Where Ulex had been burned—on all four sites on which burning had taken place.

As examples of the pastures found on the Boghall Hill between the ranges of acidity shown in Table 2, the following may be quoted as typical:—

No. 31. *Trifolium repens, Agrostis palustris, Poa trivialis*; closely grazed, *pH* 6·72.

No. 19. Agrostis, traces of *Holcus lanatus, Festuca ovina, Cynosurus cristatus, Anthoxanthum odoratum*; not grazed, *pH* 6·19.

No. 50. At 1,000 ft. elevation Agrostis, *Nardus stricta,* some *F. ovina*; grazed, *pH* 5·70.

No. 15. Nardus, Anthoxanthum, traces of *F. ovina* and *H. lanatus*; not grazed, *pH* 5·06.

No. 39. Over 600 ft. elevation, where gorse had been burned some years before, *Holcus mollis,* Agrostis, *Potentilla tormentilla*; not grazed, *pH* 4·78. Note other plants now accompanying *H. mollis,* the first to appear after burning.

No. 43. 1,000 ft. elevation, Agrostis, *F. ovina,* Anthoxanthum, traces of *Galium saxatile* and *Vaccinium myrtillus*; slightly grazed, *pH* 4·42.

No. 44. Over 1,000 ft. elevation, *Calluna vulgaris,* Vaccinium, *Aira flexuosa,* traces of Nardus and *F. ovina ;* not grazed, *pH* 3·57.

In considering Table 2 it may be seen that its records run into a far more acid region than do those of Table 1, which does not exceed an acidity of *pH* 5·0 as against *pH* 3·5—actually the limit observed was *pH* 3·57—and in this highly acid region differences in the behaviour of the grasses become apparent. *Agrostis palustris* Huds. is an un-subdivided species, under which a number of varieties may be placed; taken as a whole the species extends from the extreme alkaline to the extreme acid range, sharing its dominance in strongly acid soils with *Festuca ovina,* and giving way to Nardus in the wet peaty sites. With *Lolium perenne, Cynosurus cristatus* and locally with *Holcus lanatus* and *Anthoxanthum odoratum,* we find Agrostis as an important constituent of the permanent pastures at Seale-Hayne.

In the Boghall pastures *Anthoxanthum odoratum* persists to *pH* 4, though only frequent to *pH* 5. *Cynosurus cristatus* was not found anywhere at greater acidity than *pH* 5·5. A few plants of Dactylis and Lolium were found in an enclosed corner of a lowland field at *pH* 4·40 along with *Rumex acetosella*; they appeared to be faring poorly. Entirely wild Lolium was not found at a greater acidity than *pH* 5·5, and Dactylis not beyond the acidity of *pH* 5·8.

The regularity with which *Holcus mollis* occurred at Boghall upon all four sites where gorse had been burned, and only there, is remarkable. Apparently it is unable to maintain itself in such acid sites. At the bottom of Table 2 are shown the number of sites open to grazing—for a few of those examined were in enclosed areas; below are given those actually showing signs of having been grazed, the animals being sheep, with a few cattle and still fewer horses. A striking difference is here apparent—grazing records end at *pH* 5 to all intents, for the single records at *pH* 4·5 and 4·0 are marked as "slight," as are two out of the eight at *pH* 5 and one each at the two preceding *pH* values. On the other hand, the two pasture sites at *pH* 6·5 were marked closely grazed and well grazed.

The Boghall Hill pastures are situated upon soils of different geological origin; those on acid andesite have a peaty surface with a heather vegetation, while the basalt slopes are greener from their covering of grass. Full details of this interesting mingling of soil types have been given by Ogg and Dow (1928), who have also grouped the pastures according to reaction in this and neighbouring districts. An interesting study of the general agricultural conditions in relation to soil *pH* value has also been made by Ogg and Dow (1928). The geology and mineralogy of these soils have been examined by Hart (1929).

Permanency trials with grasses.

The soil of the Antony grass plots, Table 3, is fairly light, and its exposure and drainage ensure that it gets well baked by the sun and dried out. The sheep's fescue group might be expected to persist under these conditions in absence of serious competition from taller growth. The persistence of *Alopecurus pratensis* is rather a surprise, since it is essentially a moisture-loving grass. The fact that it matures and seeds early in the year may account for its survival. In any case the climate is not noted for its dryness, though marked periods of drought often occur in summer. *Agrostis palustris* Huds. survives, as one might expect, and the failure of *Phleum pratense* is probably due to lack of moisture.

Table 3.

Permanency trials. Antony, S.E. Cornwall. Gramineae. Sown early May, 1924. All grew and flowered. Slope facing S.S.W. *pH* 7·7–8·0.

Examined:—	30/5/'28.	2/5/'30.
1. *Lolium italicum*	None	None.
2. *L. temulentum*	None	None.
3. *L. perenne*	Some*	None.‡
4. *Festuca ovina*, L.	Plot nearly intact ...	Some areas left.
5. *Festuca ovina*, L. var. *tenuifolia*, Sibthorp.	Fair portion left ...	Some areas left.
6. *F. elatior* L. sub-sp. *pratensis*, Hackel	Persisted well over plot	Persisted well.
7. *F. elatior* L. sub-sp. *arundinacea*, Hackel.	Thriving well, in flower	Persisted well.
8. *F. ovina* L. var. *duriuscula*, Koch ...	About half has persisted	Some left.
9. *Poa pratensis* L.	None	None.
10. *P. trivialis* L.	Some left	Some left.‡
11. *P. nemoralis* L.	None	None.
12. *Alopecurus pratensis*	A few plants left ...	A few plants left.
13. *Arrhenatherum avenaceum* Beauv. ...	Some left	Some left.
14. *Anthoxanthum odoratum*	None	None.
15. *Agrostis alba*, L. var. *stolonifera* ...	Some left	Some left.
16. *Cynosurus cristatus* L.	Some left	None.‡
17. *Phleum pratense* L.	None	None.
18. *Dactylis glomerata*	Plot gone†	Some left.†

* Around old plot, none in it.

† Plot gone, but plants occur around in general. *Holcus lanatus* had appeared among the plots, also *Avena flavescens* and *Bromus mollis*.

‡ Plants occur around as natives.

The outstanding features of the plots are the thriving condition of *Festuca elatior* vars. *pratensis* and *arundinacea*, which, during the 1929 drought, were conspicuous in comparison with the rest of the plots and with the self-sown grasses on the same bank, which had been left bare in 1924 when the plots were sown.

A portion of a field facing the plots which had the grasses and leguminous plants, sown in 1924 (see Tables 3 and 6), was used for strawberries in 1925; after this it remained untouched. In May, 1928, it was found to have *Lolium perenne, Dactylis glomerata, Anthoxanthum odoratum, Holcus lanatus, Poa trivialis, Bromus sterilis, Bromus mollis, Vicia sepium, Ranunculus repens, Geranium dissectum,* and Crepis sp. The soil reaction was about *pH* 8. The area was nearly level, or sloped slightly to the north.

An adjacent portion had been used for potatoes in 1926, and then remained untouched, save by fowl, till May, 1928. It grew many weeds, notably *Convolvulus arvensis,* and was particularly rich in leguminous plants, with *Medicago lupulina* most abundant, also *Trifolium dubium* (or *minus*), *T. pratense, T. repens,* and *T. hybridum*; the soil reaction here was also about *pH* 8.

Ranges of leguminous plants.

Turning now to the leguminous plants the results, prior to 1923, given in Table 4 show that, neglecting the unwanted Ulex, wild white clover is by far the commonest native and with white clover extends into regions more acid than *pH* 6.

TABLE 4.

Leguminosae, results prior to 1923.	No. of sites.	*pH* range.
Anthyllis vulneraria, L., kidney vetch	2	7·6–8·3
Lotus corniculatus, L., bird's foot trefoil	6	7·2–8·4
Medicago lupulina, L., black medick	2	7·8–8·0
M. maculata, Sibth., spotted medick	6	6·7–7·8
Ononis arvensis, L., procumbent rest-harrow	3	7·5–8·2
Trifolium dubium, Sibth., yellow suckling clover (wet) ...	2	7·4–7·9
T. pratense, L., red clover	6	6·3–8·2
T. repens, L., white clover	5	5·8–8·2
T. repens, L., wild white clover	23	5·6–7·8
T. striatum, L., soft knotted trefoil	1	7·8
T. subterraneum, L., subterranean clover	2	7·6–7·8
Ulex europaeus, L., gorse	27	5·4–8·3

Contrary to what we find in the grasses, the limitation of the leguminous plants is rather striking, even in the less acid regions. They will indeed grow in more acid soils, but do not normally persist. Thus Karraker (1923) found in the U.S.A. that "sweet clover" (apparently Hubam clover *Melilotus alba* Desr.) gave good crops at *pH* 7·6, 6·0, 5·6, poor at *pH* 5·45, almost none at *pH* 5·05, none at *pH* 4·95, poor at *pH* 4·83, none at *pH* 4·83 (duplicates), none at *pH* 4·28. Olsen (1925) found that *Medicago sativa* (lucerne or alfalfa) and *M. lupulina* throve best in soil at *pH* 6·5–7·0, whereas at *pH* 4·0 these two plants only showed 13 and 16 per cent. respectively of the growth at optimum concentration. Hasselbach (1923) studied the soil reaction in relation to growth of *Trifolium pratense* red clover, and *M. lupulina,* also Madsen (1922), Christensen (1923), and Greve (1922). Arrhenius, too (1926), has mapped large farming areas in Sweden, with colouring corresponding to the tints of the indicators, for he saw clearly that all successful farming practice should be based on an accurate knowledge of soil reaction, especially since this is so intimately connected with nitrification, as his further work in Java (1927) has made abundantly clear.

TABLE 5.

Ranges of leguminous plants and some others. *pH* values given as 7·5, 7·0 . . . 3·5 denote the ranges 8·0–7·5, 7·5–7·0 . . . 4·0–3·5.

	Seale-Hayne.					Boghall Farm.						
pH	7·5	7·0	6·5	6·0	5·5	6·5	6·0	5·5	5·0	4·5	4·0	3·5
No. of sites	3	11	3	3	2	2	4	3	11	13	13	5
Lotus corniculatus ...	—	2	—	—	—	1	—	—	—	—	—	—
Medicago maculata ...	—	1*	1*	—	—	—	—	—	—	—	—	—
Trifolium dubium ...	1*	1	—	—	—	—	—	—	—	—	—	—
T. repens, wild white	1	3	2	2	1	2	—	—	2†	—	—	—
Ulex europaeus ...	—	—	—	—	—	—	—	—	1	2	2	—
MISCELLANEOUS.												
Calluna vulgaris ...	—	—	—	—	—	—	—	—	—	—	—	2
Galium saxatile ...	—	—	—	—	—	—	—	—	2	4	2	1
Potentilla tormentilla	—	—	—	—	—	—	—	—	—	2	—	—
Pteris aquilina ...	—	—	—	—	—	—	1	—	—	—	—	—
Rumex acetosella ...	—	—	—	—	—	—	—	—	—	3	6	—
Spergula arvensis ...	—	—	—	—	—	—	—	—	—	2	2	—
Vaccinium myrtillus	—	—	—	—	—	—	—	—	—	1	1	3
Sites exposed to grazing	3	11	3	3	2	2	4	3	11	9	11	5
Sites grazed, total ...	3	11	3	3	2	2‡	3	3	8	1	1	0
Slightly grazed only§	0	0	0	0	0	0	1	1	2	1	1	0

* Dominant. † Both grazed, *pH* 5·37 and 5·40.

‡ One closely grazed, the other well grazed.

§ Included in the totals for grazed sites in previous line.

Table 5 presents the records for leguminous plants at Seale-Hayne and Boghall Farm, also for a few native plants, which may serve as a guide to high acidity. As in Table 4, wild white clover emerges as the most important leguminous plant in our pastures. Not recorded from beyond *pH* 5·6 in Table 4, the records in Table 5 bring it to an acidity of *pH* 5·40 and *pH* 5·37—tabulated as *pH* 5·5–5·0. None of the other leguminous records in this table extend to greater acidity than *pH* 6·5, save those for *Ulex europaeus,* which goes to *pH* 4·0, and may have an important function in the fixation of nitrogen in highly acid soils. Save for very young shoots it is not, of course, susceptible of grazing.

At the bottom of Table 5 are again shown the number of sites observed to have been grazed, ending rather abruptly at *pH* 5·0; at lesser *pH* values there was slight grazing only. Thus land which is too acid for wild white clover is also too acid for grazing when the animals have any choice in the matter; their discrimination appears to be very accurate, and not governed by the presence or absence of any particular plant, but rather by a change in the quality of all the herbage.

Permanency trials of leguminous plants at Antony.

Table 6 summarises the behaviour of the sixteen species and varieties sown in May, 1924. The situation is sunny and the ground well drained, in fact rather apt to get dried out in summer. This probably accounts for the failure of wild white clover to persist. Furthermore, since the plots were not subject to grazing, save at times by fowl or stray rabbits, the taller plants had a better chance of smothering it than in a pasture.

TABLE 6.

Permanency trials, Antony, S.E. Cornwall. Leguminosae. Sown early May, 1924, in small plots, sloping S.S.W., well drained by lower ground to N. *pH* 7·7–8·0. All grew and flowered. Finally examined, May, 1930. All the species which disappeared had done so prior to 1928.

1, 2.	*Trifolium repens,* wild white clover ...	None.
3.	„ „ superfine white clover ...	None.
4, 5.	*T. pratense,* var. *giganteum,* red clover ...	Some plants.
6.	„ „ English wild red clover ...	
7.	„ „ late flowering red clover ...	Some plants, probably No. 7, var. *sativum* (Schreb.).
8.	„ „ English red clover	
9, 10.	*T. hybridum,* alsike	A few plants.
11.	*T. minus,* yellow suckling clover	None.
12, 13.	*Medicago lupulina,* yellow trefoil	A moderate amount.
14.	*M. sativa,* lucerne or alfalfa	Numerous plants, about 40 cm. high.
15.	*Lotus corniculatus,* bird's foot trefoil ...	A few plants.
16.	*Anthyllis vulneraria,* kidney vetch	A few plants.

A small amount of a variety of red clover persisted. This is a taller plant, and rather more deeply rooted, so resists drought better than white clover. *Medicago lupulina* persisted in some quantity. There is a fair amount of *M. maculata* in the district. This is important, as the nodule organism found in the roots of these plants is the same as in *M. sativa,* lucerne ; there is, therefore, no need to inoculate the soil in order to obtain a thriving crop of lucerne. The growth of lucerne was the outstanding feature of the plots. It maintained its original area almost free of intruders up to 1929. In the cold dry spring of that year it made good growth, and gave a stand about four inches high before the other leguminous plants or grasses showed any very noticeable growth. It was then eaten down badly either by slugs or poultry, but came on again, and was still flowering in September. In 1930 also the lucerne made good early growth, accompanied by yellow trefoil, with lesser amounts of the others listed in Table 6.

Fenton (1928) records lucerne as met with occasionally in Devon in hay-fields and in grass lands which are cut and grazed later in the year. In both it is very persistent. In one case an oat crop was choked out by lucerne; evidently the cultivation had been insufficient to kill the deep roots. In every instance in Devon the plant was growing in the limestone areas. In several places in Cornwall and in the Botanical Plots of the Seale-Hayne College in Devon it has given good crops, two and sometimes three cuts a year being obtained; alternatively, good seed may be produced. It would probably do well in the limestone districts in the S. of Ireland also.

Ogg and Dow (1928) examined the soils on which Cunningham (1926) grew lucerne and found that it was rarely successful in soils more acid than *pH* 6.

Determination of hydrogen ion concentration of soils.

All samples save those from Boghall Farm were examined colorimetrically against Clark and Lubs buffer solutions. For alkaline and neutral soils about one part of air-dry soil was thoroughly mixed with five of water, by weight, and was centrifuged after about one to three hours. With acid soils about two parts of water to one of soil were used. It is not permissible to filter (Atkins, 1924).

The Boghall soils were examined with the quinhydrone electrode, the voltages being corrected to 18° C. The Veibel (1923) standard buffer was used, and the quinhydrone was prepared according to the method given by Bülmann and Lund (1921). A second reading, made about ten minutes after the first, showed, as a rule, little or no difference in voltage. Most of these poor, acid soils give solutions of low conductivity (Atkins, 1924). The resistance of the extract is, therefore, high, and measurements had to be made with the sensitive type R Leeds and Northrup galvanometer, instead of with a portable lamp and scale galvanometer, as a null point indicator. Even with the sensitive instrument the readings were, in some cases, not sensitive to one millivolt. They

were, however, amply sensitive for the purpose of the research. Having seen the use of a dilute solution of potassium chloride recommended for extracting such soils, the method was tried, for the resistance of the extract is much smaller. The soils used were the first thirteen of the Boghall series and a calcareous silt from Pusa, India, marked P, as shown in Table 7. It is obvious that the use of such a solution, about 0·05 N potassium chloride when mixed, is quite inadmissible, as the error through "base exchange" is too great. The quinhydrone measurements were checked here and there by approximate colorimetric determinations, so that it is unlikely that they are affected by the error from manganese dioxide pointed out by Heintze and Crowther (1929) as occurring in some types of soils. If present in these peaty soils the manganese dioxide would have been reduced.

TABLE 7.

Comparison of *pH* values of soils extracted with water and with potassium chloride solution.

No.	Water extract.	KCl extract.	No.	Water extract.	KCl extract.
1	5·74	4·56	9	4·77	3·92
2	4·81	3·85	10	4·44	4·09
3	4·43	4·07	11	5·37	4·84
4	4·55	3·87	12	5·21	4·28
5	6·24	4·99	13	4·40	3·43 A
6	5·77	4·35	13	4·40	4·04 B
7	5·30	4·16	P	8·05	8·41
8	4·40	3·68 A			
8	4·40	3·59 B			

No. 8 A, usual procedure as in other tables, 1 c.c. saturated KCl added to soil suspension with solids.

No. 8 B, 10 c.c saturated KCl added to previous mixture.

No. 13 A, 1 c.c. saturated KCl added to about 15 c.c. turbid extract in electrode vessel.

No. 13 B, 1 c.c. saturated KCl added to soil suspension.

Summary.

1. Many British grasses are distributed over pastures differing widely in soil reaction; approximately quantitative estimations are given of a few pastures at different *pH* values.

2. *Agrostis palustris* and *Festuca ovina,* taking the species without subdivision, were found over the whole range *pH* 8 to *pH* 3·5. *Cynosurus cristatus*

and *Lolium perenne* were not found on soils more acid than *pH* 5·5, save for a few poor plants of the latter once at *pH* 4·5. *Dactylis glomerata* has much the same range. On the other hand, *Nardus stricta* was found from *pH* 3·5–6·5, *Aira flexuosa pH* 3·5–5·5, and *A. caespitosa pH* 6–7.

3. In well drained soil at *pH* 8, facing south, in Cornwall it was found that *Festuca ovina* L., *F. ov.* var. *tenuifolia* Sibthorp, and var. *duriuscula*, Koch, *F. elatior* L. sub-sp. *pratensis*, Hackel and sub-sp. *arundinacea*, Hackel persisted well for six years. *Lolium perenne* disappeared as a plot, also *Cynosurus cristatus*, *Anthoxanthum odoratum*, and *Dactylis glomerata*, while *Lolium italicum*, *L. temulentum*, *Poa pratensis*, *P. nemoralis*, and *Phleum pratense* disappeared altogether.

4. Of leguminous plants *Ulex europaeus* extends from *pH* 8–*pH* 4, and may be an important source of nitrogen fixation in the more acid soils. *Trifolium repens*, wild white clover, is the most important leguminous constituent of acid pastures, in which, however, it is not found in soils more acid than *pH* 5. *T. pratense*, red clover, is rare beyond *pH* 6, as are most of the other leguminous plants, some not having been found beyond *pH* 7.

5. In the site mentioned in § 3, the persistence of *Medicago sativa*, lucerne, over the six years was the outstanding feature. *M. lupulina* also persisted, though not so abundantly, as did a lesser amount of *T. pratense*, red clover, *T. pratense* var. *giganteum*, *T. hybridum* (alsike), *Lotus corniculatus*, and *Anthyllis vulneraria*. *Trifolium repens* and *T. minus* died out.

6. When allowed to roam freely sheep and cows graze closely on herbage growing in soil at *pH* 6·5, and will graze on most sites less acid than *pH* 5. Between *pH* 5 and 4·5 out of nine sites examined only one was slightly grazed, and between *pH* 4·5 and 4·0 only one, also slightly, out of eleven, and none below *pH* 4. To all intents grazing ceases at *pH* 5. The observations were made in July in S. of Scotland.

7. The use of a neutral solution of potassium chloride with which to obtain soil extracts for *pH* determinations leads to large errors through base exchange even when the final concentration of the chloride is only about 0·05 N.

Measurements of soil reaction were made, throughout this paper, colorimetrically, using Clark and Lubs' standard buffer solutions and centrifuged soil extracts, or by the use of the quinhydrone electrode with Veibel standard buffer.

The work described was carried out partly at the Seale-Hayne College, partly at the Boghall Experimental Farm, at Antony, Cornwall, and at the Marine Biological Laboratory, Plymouth.

We desire to express our thanks to Messrs. Sutton & Sons and to Messrs. Carter for kindly presenting to us the seeds of these grasses and leguminous plants sown in the permanency trials and for their assistance in other ways.

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No. 47.

A STUDY OF FUNGI FOUND IN BUTTER.

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(Plates 22 and 23.)

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In the course of an investigation into the causes of deterioration of butter made from sweet cream, eight half-pound samples of butter were forwarded by the Butter-Testing Station, Department of Agriculture, Irish Free State, for examination each month, commencing October, 1929. These eight samples were taken from the four boxes scoring highest for flavour and the four boxes scoring lowest for flavour at the first surprise inspection held each month. The percentage of salt in the butter samples varied from nil to 2·0 per cent., with the exception of a few samples containing from 2·0 per cent. to 3·0 per cent. salt.

The samples of butter for these butter inspections are taken as follows:—Inspectors pay surprise visits to creameries, take and seal a 56 lb. box of butter at each, and leave instructions to have them forwarded to the Butter-Testing Station, Dublin. These boxes are held for a period of twelve days, and then judged and scored.

The samples of butter, on the day of arrival at University College, Cork, were cut with a sterile knife, about 30 grams were taken from the interior, put into a sterile bottle, melted at 37° C., and 0·1 c.c. and 0·01 c.c., respectively, of the mixed sample plated in duplicate on nutrient lactose agar, to which sufficient lactic acid had been added to give the media a *pH* of 3·5 in order to prevent bacterial growth. The Petri dishes were then incubated for a week at 21° C. before examination. At each examination a survey was made of the different types of moulds found, and a study made of each type on its first appearance. The most prevalent species found, in order of frequence, were Penicillium, *Oidium lactis*, Aspergillus, Cladosporium, Phoma. The other species were rarely found, and there were usually only 10 or 20 present per c.c. of butter examined.

Dr. G. Van B. Gilmour, Dairy Bacteriologist, Butter-Testing Station, Department of Agriculture, Dublin, also kindly forwarded cultures of moulds isolated by him from butter for identification.

The moulds for cultivation purposes were grown on nutrient lactose agar *pH* 7·0, or on Czapek agar *pH* 6·9, or on Richards' agar (1). The Czapek solution, without the addition of agar, was used for the cultivation of the moulds in liquid, and for the study of heat tolerance and salt tolerance. The Czapek solution without the addition of agar had a *pH* of 7·5, but, as all the moulds studied grew well in it, the *pH* was not corrected to 7·0. All the *pH* figures were obtained colorimetrically by the use of a comparator, using a suitable indicator, e.g., Brom-thymol blue was used for the range 6·0 to 7·6.

The study of mould growth at low temperatures was carried out by inoculating in duplicate on nutrient lactose agar slopes, incubating at 21° C. until growth was well started, marking area of growth, and incubating one set of nutrient lactose agar slopes at 5° C. or 8° C. for three weeks in a humid atmosphere, then examining, noting if area of growth had increased, and comparing with the second set of slopes which had been held at 21° C. as controls.

Heat tolerance was studied by inoculating into Czapek solution contained in 6″ × 1″ test tubes, one-third full, heating to the desired temperature, incubating at 21° C. for two weeks, and noting if growth occurred. The *pH* of the solution was noted after period of incubation.

Salt tolerance was studied by adding 3 per cent., 5 per cent., 10 per cent., 15 per cent., and 20 per cent. of sodium chloride to Czapek solution, inoculating with a culture of the mould, incubating at 21° C. for two weeks, observing if growth occurred, and noting the *pH* before and after period of incubation.

Liquefaction of gelatine was determined by making a stab inoculation into nutrient gelatine, incubating at 21° C., and examining daily for ten days. The production of diastase by the mould species was determined by making a streak inoculation on lactose nutrient agar containing 0·1 per cent. soluble starch, incubating at 21° C., until there was marked growth, then flooding the plate with Lugol's iodine solution, and determining the size of the area that did not stain on the addition of the iodine solution. Diastase production is classed as either absent, feeble, fair, or good.

Growth in milk was determined by inoculation into litmus and calcified milk, and incubating at 21° C. for a period up to two weeks.

Where the morphology of a mould species is not described a reference is given to its description in our previous paper (2).

It is noted that the growth of moulds is affected by various factors. Tomkins (3) has shown that the rate of germination varies for different fungi, and that the further removed the temperature is from the optimum the slower the rate of germination; also, that the range of humidities over which germination is possible varies with the temperature, and that the further the tem-

perature is removed from the optimum the narrower is the range of humidities allowing germination.

Brooks and Hansford (4) observed that the spores of all mould fungi found on cold-store meat, notably *Cladosporium herbarum* (*Hormodendron cladosporioides*), *Penicillium expansum*, and *Thamnidium* spp., remain alive after being subjected to a temperature of – 6° C. for two years, and that *Mucor* spp. will grow at 0° C., or just above.

Joslyn and Cruess (5), studying various species of Penicillium, found that the salt tolerance was related to the *pH* of the medium. The lower the *pH* the less the amount of salt necessary to inhibit growth. They give the following figures for the percentage of salt required to inhibit growth with varying *pH* :—

pH	2·5	3·2	5·1	6·3
Percentage of salt ...	0	10	18	16

They also found that the thermal death-point was influenced by the *pH*, salt concentration, and the amount of inoculum used. They found that the death temperature of a penicillium species was lowered to 55° C. from 75° C. by the addition of 10 per cent. salt, and was lowered to 50° C. from 75° C. by altering the *pH* to 2·75.

One of us (6) has studied the influence of *Oidium lactis* on the keeping quality of butter made from the ripened cream containing 1·5 to 2·1 per cent. NaCl, and stored at – 6° F. for from six to seven months. He found that *Oidium lactis* did not survive cold storage.

That moulds are influenced by the percentage of NaCl in butter is also shown by Macy (7), who found that, when mould estimations were made of butter before and after cold storage for periods of one to nine months, the moulds decreased to a greater extent in the salted butter than in the unsalted. He gives the following table :—

	Mould Count.		
	Per cent. increase.	Per cent. no change.	Per cent. decrease.
Salted butter ...	22·6	12·6	64·8
Unsalted butter ...	85·4	4·0	10·6

Macy notes that the addition of 1 per cent. NaCl to the butter had an inhibitive effect. In judging the salt tolerance of moulds it must be remembered that, assuming the average amount of water in butter to be 15·5 per cent., this would be equal to 6·45 per cent. NaCl in the serum. Orla Jensen (8) states that *Oidium lactis*, *Penicillium glaucum*, and *Cladosporium butyri* grow better and more quickly in unsalted than in salted butter. Thom and Shaw (9) state that species of Oidium, Alternaria, and Cladosporium cannot develop in butter containing 2·5 per cent. NaCl. The following fungi are stated by Clinton (10)

to have been found in mouldy unsalted butter:—Mucor, Alternaria, *Penicillium roqueforti, Oidium lactis,* Epicoccum; and Morgan (11), who has made a study of moulds in unsalted butter, lists the following species:—*Penicillium glaucum,* Stemphylium, *Fusarium lactis, Oidium lactis, Cladosporium herbarum, Cladosporium butyri.* He states that the spores of *Oidium lactis* will remain virile for about six weeks after manufacture, and that after six weeks the mould gradually dies out. Morgan states that germination of Stemphylium spores had never occurred at a temperature higher than 70 °C., and that moulds of the Stemphylium type are capable of germinating, and growing well in media containing 5 to 7 per cent. of NaCl; also that spores of Stemphylium mould inoculated into butter showed no signs of growth when the butter was kept at 3° C. to 5° C. for three months. Morgan found that spores of *Fusarium lactis* did not germinate from cultures heated higher than 60° C., and that they are capable of germination in media containing 8 per cent. NaCl. He found that spores of *Penicillium glaucum* frequently germinated after heating to 75° C., and that the spores could germinate in media containing 7 per cent. NaCl, but rarely in media containing 8 per cent. NaCl. Morgan found that spores of *Oidium lactis* rarely germinated from cultures heated to 60° C. or over, and that no germination was found in media containing more than 4 per cent. NaCl. He states that spores of *Oidium lactis* will not germinate when kept at 5° C. for three months, but that the mould will germinate in a week at 10° C. Morgan states that spores of *Cladosporium* spp. will not germinate if heated to 70° C. or over, and will germinate in a medium containing 7 per cent. NaCl. Macy (17) made a study, using ten species of mould isolated from butter, of some of the factors influencing the growth of mould in butter, and concluded that, as an ample food and water supply is provided, the growth of moulds in butter appears to depend largely upon the species of mould, the humidity of the atmosphere, the supply of oxygen, the temperature of storage, time, and the concentration of salt.

These influences may act separately or collectively.

Aspergillus fumigatus Fres. (1, p. 129) (Pl. 22, figs. 2 and 4, Pl. 23, fig. 1).

Colonies on Czapek agar velvety or floccose, green to dark green, or black when old. Reverse of colony uncoloured or rose red on lactose agar slopes, and also in Czapek solution when heated to 70° C.

Conidiophores short, crowded, greenish coloured, rising from submerged or aerial hyphae, septate or unseptate. The vesicle is flask-shaped, 10μ in diameter (Thom (1, p. 129) states 20μ to 30μ is usual size), fertile on upper half. The sterigmata are in one series, varying in size, and form solid columns. The condidia are dark green, globose, 2–3·5μ in diameter. Cultures grow well at 37° C. The forms and measurements of *A. fumigatus* are very variable; the heads, however, have a characteristic clavate shape, and are much larger than the somewhat similar heads formed in old cultures of *Aspergillus terreus.*

Milk Cultures.—Good growth, coagulation, fine curd. No odour.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 80° C. No apparent growth of colony when kept three weeks under 5° C. No red coloration in medium while in cold storage: this, however, appeared when the culture was transferred to a cupboard at room temperature (18° C.), when there was normal growth.

Salt Tolerance.—Growth in Czapek solution containing 10 per cent. NaCl fairly strong; practically no growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—Little or no change when grown for two weeks in Czapek solution with or without the addition of salt.

Gelatine.—Slight liquefaction in 10 days.

Diastase Production.—Fair.

Aspergillus luteo-niger (Lutz) (1, p. 166) (2, p. 315).

Milk Cultures.—Acid, coagulation followed by rapid digestion.

Heat Tolerance.—Growth when heated to 75° C. No growth when heated to 80° C. Slight growth when kept at about 8° C. for three weeks. When kept at 5° C. for three weeks there was no appreciable increase in size of colony.

Salt Tolerance.—Good growth in Czapek solution containing 10 per cent. NaCl. Little or no growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution containing 10 per cent. salt for two weeks the *pH* changes to 5·0.

Gelatine.—Liquefaction in 10 days.

Diastase Production.—Good.

Aspergillus sydowi (Bainer and Sartory) (1, p. 147).

Colonies greenish blue, velvety, with aerial hyphae interlacing and trailing, reverse of colony brick red to orange, becoming dark in old colonies. Stalks usually arise from submerged hyphae, and are up to 500μ × 4–8μ, colourless, smooth, and thick-walled; heads globose, vesicles, 12μ–20μ in diameter, sterigmata in 2 series, conidia globose 3μ–3·5μ in diameter, spinulose. Small heads sometimes present, or penicillate clusters of branched sterigmata on short conidiophores, or single-branched sterigmata sessile on trailing hyphae.

Milk Cultures.—Good growth, acid, coagulation with digestion of curd.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—Fair growth in two weeks in Czapek solution containing 10 per cent. NaCl; little or no growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution containing 10 per cent. NaCl *pH* of medium = 4·0.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Aspergillus terreus Thom (1, p. 150) (2, p. 316) (Pl. 22, figs. 3 and 5).

In addition to the description given in Thom (1), it was noted that in old cultures columnar heads were formed resembling *Aspergillus fumigatus,* but of a smaller size (Pl. 22, fig. 3).

Milk Cultures.—Thick clotting of milk in 3 days. No apparent mycelial growth.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—Good growth in Czapek solution containing 12 per cent. NaCl. Good growth on bottom of flask in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution, with and without the addition of NaCl, the *pH* of the medium varied from 6·2 to 6·7.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Aspergillus glaucus group Link var. (1, p. 101) (Pl. 22, fig. 1, A, B, and C).

Colonies at first yellowish green, later green, velvety, with typical glaucus group head, sterigmata in one series, conidia rough, 7μ × 5μ. Sterigmata sometimes branched, as in fig. 1, B, to form secondary heads.

Heat Tolerance.—No growth when heated to 75° C.

Salt Tolerance.—Growth in Czapek solution containing 5 per cent. NaCl. No growth in Czapek solution containing 10 per cent. NaCl.

pH.—Slight or no change in reaction when grown in Czapek solution for two weeks.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Penicillium brevi-compactum Dierckx var. (12, p. 295) (Pl. 22, fig. 6).

Colonies on nutrient lactose agar are green and zonate. When grown on Czapek agar they agree with Thom's description (12, p. 295):—"Grey-green to fairly deep green, velvety, loose, long stalked, on a thin basal aerial felt up to 1 mm. in depth in centre, margin of conidial area velvety with narrow white margin."

The heads show the characteristically short compact base with divergent sterigmata and conidial chains (see Pl. 22, fig. 6). Conidiophores 4–6μ in diameter, very slightly pitted penicillus, with short primary branch, crowded, and more or less divergent metulae, and sterigmata with loosely parallel, then

tangled chains of conidia 3–5μ in diameter. Our cultures showed spores slightly over the 5μ in diameter. Similar colonies on Richard's agar.

Milk Cultures.—Total digestion, alkaline reaction.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—Slight growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution with and without the addition of NaCl $pH = 6{\cdot}0$.

Gelatine.—Liquefaction in 10 days.

Diastase Production.—Feeble.

Penicillium Johannioli Zaleski (12, p. 391).

This and the following species (*Penicillium cyclopium*) belong to the blue-green subdivision of the Fasciculata group (Thom, 12, p. 391). In the *Penicillium Johannioli* series the zones are narrow, and crowded at the margin, yellow on the reverse, but the colour may be reduced, or even become purplish or black with age.

Colonies on nutrient lactose agar are blue-green, changing when old to smoky colour, at first azonate, then zonate, underside pale to deep yellow in old lactose agar colonies, showing crowded zones, not wrinkled in our cultures—but, according to Thom, may have a few radiate but delicate wrinkles, with the mycelium giving a typically radiate appearance. Conidiophores 400–500μ × 3–4μ, straight, simple, or occasionally branched. Penicillus mostly 40μ–55μ long, with 2 or 3 branches 18μ–32μ × 3μ–4μ, the walls may be smooth or slightly roughened, metulae 10–13μ × 2·5μ–3μ in groups of 4–6, commonly vesicle-like at apex, uneven in length.

Sterigmata about 9μ–10μ × 2μ–2·2μ to 4μ × 2·2μ–3·5μ, mostly subglobose, some ovate, smooth, not persistently adherent in chains or masses.

Milk Cultures.—Coagulation followed by digestion.

Heat Tolerance.—No growth after being heated to 70° C. This mould grew when kept at 5° C. for three weeks.

Salt Tolerance.—Very good surface growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution the *pH* of the medium altered to 5·0. When grown for two weeks in Czapek solution containing 10 per cent. and 15 per cent. NaCl, respectively, the *pH* was 4·0.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Penicillium cyclopium Westling var. (12, p. 384).

Differs from the *Penicillium Johannioli* series in having the zonation of the colony appearing late, and remaining usually indistinct. On Czapek agar the

zonation appears late, the colonies are velvety, thin at the margin, and the centres are sometimes overgrown with white mycelium; the marginal area changes from white during the growing period to a bluish-grey green. The reverse varies from pale yellow when young to purplish shade in centre when old (Czapek agar), or purplish orange (nutrient lactose agar); outer edges in Czapek agar show slight greenish tinge. There is a definite characteristic odour. Conidiophores with rough walls, 3μ in diameter. Penicillus long, about 150μ (Thom = 45–120μ), has a long main stalk, and long appressed branch, or branches, carrying metulae in verticels, sterigmata on end of metulae, conidia are smooth, green, globose, about 3μ in diameter.

Milk Cultures.—Alkaline digestion.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—Grows in Czapek solution containing 10 per cent. NaCl. Yellowish discolouration on under-surface. No growth in Czapek solution containing 15 per cent. NaCl.

pH.—When grown in Czapek solution with and without the addition of NaCl four weeks $pH = 4{\cdot}0$.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Good.

Penicillium sartoryi var. Thom (12, p. 233).

Colonies at first white, then a greenish yellow. Conidiphores long, with an apical group of diverging branches having vesicular apices, from which spring sterigmata and conidia, the latter in a long chain. Sterigmata may arise singly from the fertile hyphae without the presence of a conidiophore, and are irregular in size. Conidia smooth, 4–5μ × 2μ.

Milk Cultures.— Coagulation.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—Slight growth in Czapek solution containing 10 per cent. salt. No growth in Czapek solution containing 15 per cent. NaCl.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Penicillium spinulosum Thom var. (12, p. 183).

Colonies at first green, later smoky brown, under-surface uncoloured, aerial hyphae floccose. Conidiophores long, 150μ–300μ × 3μ–5μ, and bear a single verticel of sterigmata 9·5μ × 11μ–2·3μ. Penicillus is loose column of chains up to 500μ long, conidia are oval to globose, and with thin walls, at first greenish, later a smoky brown, 3·2μ–3·5μ × 3·6μ–4μ.

Milk Cultures.—Coagulation followed by digestion of curd.

Heat Tolerance.—No growth when heated to 65° C. No growth when held at 5° C.

Salt Tolerance.—No growth in Czapek solution containing 10 per cent. NaCl.

pH.—When grown in Czapek solution *pH* of the medium altered to 6·4.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Good.

Gliocladium corda (12, p. 498) (Pl. 22, fig, 7, A and B).

Colonies on Czapek agar velvety-looking, white to dirty pinkish-yellow, ochraceous when mature. Grows in small spreading tufts. Reverse of colony pale yellow. When cultured in flask turns Czapek solution bright yellow. The conidial fructifications are upright, and resemble a Penicillium in structure and production of conidia, except that the conidia are bound by mucus into balls. The conidia are smooth, hyaline, and elliptical, 5μ–7μ × 3μ, and borne on acuminate sterigmata variable in length, generally 10μ–15μ long, springing from conidiophores of variable length, about 3μ in thickness. Considerable confusion exists in the Gliocladium group. Judging by conidial measurements and colour this species described appears to approach *Gliocladium luteolum* von Hohnel. (12, p. 509.)

Milk Cultures.—Alkaline digestion.

Heat Tolerance.—Growth when heated to 75° C. No growth when heated to 80° C. No growth when kept at 5° C. for three weeks.

Salt Tolerance.—When grown in Czapek solution containing 3 per cent. NaCl at end of 7 days a filmy, fluffy, submerged growth, having a dirty white colour. Also a thin growth on surface, with the older parts yellowish. When grown in Czapek solution containing 5 per cent. NaCl a good growth in tiny patches on surface, and submerged budding in cladosporium fashion. Slight growth in Czapek solution containing 10 per cent. NaCl, and little or no growth in Czapek solution containing 15 per cent. NaCl.

pH.—Little or no change when grown in Czapek solution for two weeks with and without the addition of NaCl.

Gelatine.—One-half liquefaction in 10 days.

Diastase Production.—Good.

Trichoderma lignorum Tode (15, vol. 8, p. 110) (Pl. 22, fig. 8, A, B, and C).

Floccose, lumpy, creeping mycelium, at first white, changing through yellow to green. Older cultures powdered over with white sterile mycelium. Conidia rounded, smooth, green, and measure 2·5μ–3μ in diameter, and borne in heads on ends of short conidiophores (Pl. 22, fig. 8A). Chlamydospores about 10μ in diameter (fig. 8, B and C), were found in enormous numbers in the lactose slopes kept below 8° C. These were observed also in the slope kept at 21° C., but in the latter case they were few in number.

These structures had thick hyaline walls, contained refractive bodies, and were either terminal or intercalary on the hyphae. Horne and Williamson describe similar bodies as "macrospores" in their *Eidamia viridiscens,* which Thom considers to be a *Trichoderma species* (Ref. 12, p. 542; Ref. 13, p. 396).

Milk Cultures.—Partial digestion with production of acid in 5 days.

Heat Tolerance.—Growth when heated to 80° C. No growth when heated to 85° C. When kept under 8° C. good growth of sterile mycelium. When kept under 5° C. no apparent growth.

Salt Tolerance.—Poor growth in Czapek solution containing 12 per cent. NaCl. No growth in Czapek solution containing 15 per cent. NaCl.

pH.—Reaction of medium unaltered when grown in Czapek solution with and without the addition of NaCl.

Gelatine.—Partial liquefaction—one-quarter to one-third in 10 days.

Diastase Production.—Good.

This mould was also found growing on deal planks imported for building purposes.

Graphium penicillioides Corda (14) (Pl. 22, fig. 9, A, B, and C).

Appeared as fluffy cushions of white mycelium, conidia appear on branched or unbranched conidiophores (fig. 9C); sometimes they may be produced from mycelium without the presence of conidiophore. Conidia are longish, and variable in size. Some thickened hyphae appear in the colony, and become dark in colour—these also bear conidia, and later from them the graphium type of fructification arises. The length of time of production varies considerably; they are slower on lactose agar than on Czapek or Richard's agar (fig. 9, C).

The graphia (Pl. 22, fig. 9, A and B) are short, stout black cylindrical pillars, bearing a spherical milky white head. Each one arises from swollen cells in mycelium, a thick strand is formed, and the hyphae forming it may be twisted, from the tip of which branch off small colourless conidia. The liquid in which the spores are held is mixable with water. Perithecia did not appear in our cultures.

Milk Cultures.—Strong growth, digestion of curd, acid reaction.

Heat Tolerance.—Slight growth of the cladosporium type when kept for three weeks at 5° C. Better growth when kept at 8° C. for three weeks.

Salt Tolerance.—No growth in Czapek solution containing 20 per cent. NaCl.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Fair.

Coniosporium arundinis Corda (15, vol. 8, p. 558) (Pl. 22, fig. 10, A and B; Pl. 23, fig. 2).

A difficult form to recognise, as growth in media is entirely different from form found on trees; the characteristic spores, with hyaline rim, however, identify it as Coniosporium species. Creeping septate, white mycelium, with

olive green spores, about 6μ long (see Pl. 22, fig. 10B). Spores, which are circular, or subangular in outline and lenticulate, are borne at the tops of conidiophores, each attached by a small outgrowth, which becomes gelatinous and disappears, so that spores have appearance of being borne in heads or clumps. Later all mycelium disappears, and black spots are seen under the medium later: these may lose their rounded appearance and coalesce, forming long streaks (Pl. 23, fig. 2); later they reach the upper surface of the medium. They are then seen to be masses of olive green spores, up to 6·6μ long.

Milk Cultures.—Acid, coagulation followed by digestion.

Heat Tolerance.—No growth when heated to 70° C. Slight growth when kept at 5° C. Fair growth when kept at 8° C.

Salt Tolerance.—Fair growth in Czapek solution containing 12 per cent. NaCl. No growth in Czapek solution containing 15 per cent. NaCl.

pH.—Reaction unaltered when grown in Czapek solution with and without the addition of NaCl.

Gelatine.—Partial liquefaction in 10 days, brownish transparent "acervuli" on surface of medium and sides of tube.

Diastase Production.—Good.

Fusarium species.—Strain A, from butter; Strain B, from butter, microconidial stage; Strain C, from milk.

Fusarium.—Strain A (Pl. 22, fig. 11, A, D, E, and F).

Obtained from sample of butter. Spores sickle-shaped, sharply pointed at each end up to 3 septa (22–35μ × 3·5–4·5μ); sometimes with continuous microconidia. Dr. Ashby (Imp. Bur. Myc.) reports that this form produces on potato mush agar and Quaker oats agar, a carmine plectenchyme, dark blue sclerotia, and creamy sporodochia; while on rice it gives a growth carmine above and brownish yellow below, with sclerotia; chlamydospores are absent or scanty. It appears to be intermediate between sections *Discolor* Wr. and *Lateritium* Wr., the conidia being like those of *F. salicis* Fuck, but that species has not been recorded with carmine plectenchyme.

Milk Cultures.—Acid, coagulation followed by digestion.

Heat Tolerance.—No growth when heated to 70° C. This mould grew when kept at 5° C.

Salt Tolerance.—Growth in Czapek solution with the addition of 12 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—Little or no change when grown in Czapek solution with and without the addition of salt.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

This species was isolated from a sample of butter which had developed reddish patches on surface.

Fusarium.—Strain B (Pl. 22, fig. 11c).

Microconidial stage, which always produced single microconidia $6\mu \times 3\mu$ on all media. Very few macroconidia; these were three septate, and very pointed at the ends. On gelatine, under-surface of colony showed pink colour, on Czapek agar a more orange pink.

Milk Cultures.—Litmus milk decolourised.

Heat Tolerance.—Growth after being heated to 65° C. Slight growth when heated to 70° C. No growth when heated to 75° C. Very slight growth when held at 5° C.

Salt Tolerance.—In Czapek solution containing 3 per cent. NaCl mycelium breaks into rounded spores, fair growth in Czapek solution containing 12 per cent. NaCl, very slight in 15 per cent. NaCl. No growth in 20 per cent. NaCl.

pH.—Little or no change when grown in Czapek solution with and without the addition of NaCl.

Gelatine.—Three-quarters liquefaction in 10 days.

Diastase Production.—Feeble.

A culture of this species was sent to Mr. S. F. Ashby, of the Imperial Bureau of Mycology, who stated that Dr. H. W. Wollenweber had determined it as *F. reticulatum* Mont. (Ann. Sci. Nat., 2nd Ser., **20**, 379, 1843; Wollenweber's Fusaria autographiae delineata, 119–121 and 938, 939). This species is also recorded in Sacc. syll. × 726 as *F. ampelodesmi* Faut et Roum. Other records are on *Beta vulgaris* in Germany, and *Cucumis melo* in Denmark.

Fusarium.—Strain C. (Pl. 22, fig. 11b).

In addition to these, a Fusarium was obtained from milk; this was not reported in our previous paper. The macrospores were more sausage-shaped than those of the Fusarium species found in butter, 5 septate, and not pointed at the ends; spores were larger than the butter form, being $30\mu \times 5\mu$–$6{\cdot}6\mu$ in length.

Milk Cultures.—Very high white fluffy growth with production of acid, coagulation followed by digestion of curd.

Heat Tolerance.—No growth when heated to 70° C. No apparent growth of colony when kept for three weeks at 5° C.

Salt Tolerance.—Fair growth in Czapek solution containing 12 per cent. NaCl; very slight growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—Little or no change when grown in Czapek solution with and without the addition of salt.

Gelatine.—$\frac{1}{3}$ liquefaction in 10 days.

Diastase Production.—Feeble.

Alternaria spp. (Pl. 23, fig. 3).

The stem and spores are rough, and a brown colour, with colourless beaks between the irregularly sized spores, which are in chains. The form belongs to the *A. tenuis* group as defined by Mason, although the spores are sometimes oval rather than obclavate.

Milk Cultures.—Acid, coagulation followed by slow digestion.

Heat Tolerance.—Growth at 70° C. No growth at 75° C.

Salt Tolerance.—Very slight growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown in Czapek solution *pH* of the medium altered to 5·5.

Gelatine.—Slow liquefaction in 12 days.

Diastase Production.—Feeble.

A species of Alternaria was found growing on deal planks imported for building purposes.

Stemphyllium spp. (15, vol. 9, p. 215) (Pl. 22, fig. 12, A and B).

This form resembles *S. ericoctonum* A. Br. and de Bary, but the spores are longer. The hyphae are very jointed, and spores (22–38μ × 8–13μ) smooth, and brownish green in colour.

Milk Cultures.—Alkaline reaction and digestion of curd.

Heat Tolerance.—No growth when heated to 70° C. When kept at 8° C. there was good growth of sterile mycelium. No growth when kept at 5° C.

Salt Tolerance.—Growth in Czapek solution containing 10 per cent. NaCl, slight growth in Czapek solution containing 15 per cent. NaCl. and no growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown for two weeks in Czapek solution *pH* = 6·6.

Gelatine.—One-third liquefaction in 10 days.

Diastase Production.—Negative or slightly feeble.

Stemphyllium ericoctonum var. (Pl. 23, fig. 4).

A variety of this species was also found in which the spores are borne in short chains, and are darker and slightly smaller in size, being 21–36μ × 7–9μ. It is thought to be a strain of *S. ericoctonum*.

Milk Cultures.—Alkaline reaction and digestion of curd.

Heat Tolerance.—Growth when heated to 65° C. No growth when heated to 70° C. No growth when kept at 5° C. for three weeks.

Salt Tolerance.—Slight growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—When grown for two weeks in Czapek solution *pH* = 6·6.

Gelatine.—One-third liquefaction in 10 days.

Diastase Production.—Negative.

Torula Pers. Sp. (Pl. 22, fig. 13).

A Torula species was found on one occasion with spores 4 × 3·3μ.

Salt Tolerance.—Growth in Czapek solutions containing 5 per cent. and 10 per cent. NaCl. No growth in Czapek solution containing 15 per cent. NaCl.

Diastase Production.—Feeble.

Phoma spp.

Two Phoma spp. were found frequently, but no work was done with them, as they are being investigated by another member of the Botanical Department.

Oidium (*Oospora*) *lactis* Fresen (2, p. 311).

This form was found frequently; generally growing in close contact with yeasts, and difficult to separate into pure culture.

Milk Cultures.—Acid, coagulation and digestion.

Heat Tolerance.—No growth when heated to 60° C.

Salt Tolerance.—Growth in Czapek solution containing 5 per cent. NaCl. Slight growth in Czapek solution containing 10 per cent. NaCl. No growth in Czapek solution containing 15 per cent. NaCl.

Gelatine.—No liquefaction in 10 days.

Diastase Production.—Negative.

Acrostalagmus cinnabarinus Corda (2, p. 312).

Milk Cultures—Alkaline reaction and digestion.

Heat Tolerance.—Growth when heated to 70° C., as a white submerged film. No growth when heated to 75° C. No apparent growth when kept three weeks at 5° C.

Salt Tolerance.—No growth in Czapek solution containing 15 per cent. NaCl.

pH.—Slight or no alteration of reaction when grown in Czapek solution with and without the addition of NaCl.

Gelatine.—Liquefaction in 10 days, brick-red colouration in medium.

Diastase Production.—Good.

Botrytis cinerea Pers. (2, p. 315).

Milk Cultures.—Acid, coagulation, followed by digestion.

Heat Tolerance.—Growth when heated to 65° C. No growth when heated to 70° C. When kept at 5° C. growth normal, but with fluffy sterile mycelium.

Salt Tolerance.—Little or no growth in two weeks in Czapek solution containing 10 per cent. NaCl.

pH.—When grown in Czapek solution the *pH* of the medium altered to 6.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Fair.

Cladosporium spp. (Syn. *Hormodendrum*). (2, p. 313).

We consider with Brooks (4) that the distinction between *Cladosporium* and *Hormodendrum* is a question of the amount and character of the budding of the first formed conidia, and that the two forms gradually merge into one another. Owing to the difficulty of identification, since the type of growth varies with the medium used for cultivation, we were not able to identify the different species met with in the course of this work, but they divided into two chief types—(*a*) a *Cladosporium* type, with larger cells and conidiophores not so complicated as the (*b*) *Hormodendrum* type, with a higher degree of branching in conidiophores and smaller cells.

Milk Cultures.—Thick characteristic growth, partial digestion with production of acid.

Heat Tolerance.—No growth when heated to 60° C.

Salt Tolerance.—Fair growth in Czapek solution containing 10 per cent. and 12 per cent. NaCl. Slight growth in Czapek solution containing 15 per cent. NaCl. No growth in Czapek solution containing 20 per cent. NaCl.

pH.—Little or no change in *pH* when grown in Czapek solution with or without the addition of NaCl.

Gelatine.—Gelatine 50 per cent. liquefied in 10 days.

Diastase Production.—Fair.

Mucor racemosus: Fres. (2, p. 314).

Milk Cultures.—Milk curdled in 48 hours, with decolourisation of the litmus, except on surface, followed by slow digestion of the curd.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C.

Salt Tolerance.—No growth in Czapek solution containing 15 per cent. NaCl.

pH.—When grown in Czapek solution the *pH* of the medium became 6·8.

Gelatine.—Liquefaction in 10 days, green colouration on under-surface.

Diastase Production.—Feeble.

Mucor corymbifer (2, p. 314).

Milk Cultures.—Coagulation with production of acid and soft curd, and separation of whey.

Heat Tolerance.—Growth when heated to 70° C. No growth when heated to 75° C. This mould grew well when kept at 5° C.

Salt Tolerance.—Growth in two weeks in Czapek solution containing 10 per cent. NaCl. Chlamydospores formed in Czapek solution containing 3 per cent. and 5 per cent. NaCl.

pH.—Little or no change in reaction of Czapek solution with and without addition of NaCl.

Gelatine.—Partial liquefaction in 7 days. The mycelium growing in the liquid portion showed an oidium condition, with a green colouration on the under-surface.

Diastase Production.—Feeble.

Stysanus microsporus Sacc. (2, p. 314).

Milk Cultures.—Good growth, but no production of conidial heads, acid reaction.

Heat Tolerance.—No growth when heated to 70° C. No growth when kept at 5° C. for three weeks.

Salt Tolerance.—Growth in Czapek solution containing 10 per cent. NaCl. Little or no growth in Czapek solution containing 15 per cent. NaCl.

pH.—When grown in Czapek solution the *pH* of the medium altered to 6·6.

Gelatine.—Partial liquefaction in 10 days.

Diastase Production.—Feeble.

Sporotrichum carnis (4 and 2, p. 312).

Milk Cultures.—Thin papery growth, slow coagulation followed by digestion.

Heat Tolerance.—No growth after being heated to 60° C. When kept three weeks at 5° C. fairly good growth, pure white colour.

Salt Tolerance.—Good growth in two weeks in Czapek solution containing 5 per cent. NaCl, slight in Czapek solution containing 10 per cent. NaCl, and no growth in Czapek solution containing 15 per cent. NaCl.

pH.—Little or no change in reaction of Czapek solution with or without the addition of NaCl.

Gelatine.—Gelatine 50 per cent. liquefied in 10 days.

Diastase Production.—Feeble.

Trichothecium roseum Link (2, p. 314).

Milk Cultures.—Good growth, production of acid, and finally digestion of the milk.

Heat Tolerance.—Growth when heated to 65° C., no growth after being heated to 70° C.

Salt Tolerance.—Good growth in Czapek solution containing 5 per cent. NaCl; slight growth in Czapek solution containing 10 per cent. NaCl and 12 per cent. NaCl. Little or no growth in Czapek solution containing 15 per cent. NaCl.

pH.—*pH* unaltered when grown for two weeks in Czapek solution with and without the addition of NaCl.

Gelatine.—Gelatine 50 per cent. liquefied in 10 days.

Diastase Production.—Fair.

Chaetomium bostrychoides Zopf (16) (Pl. 22, fig. 14).

This form, which is an extremely variable one, was found on one occasion, perithecia appearing in the cultures. The perithecia are steel grey, oval-shaped, but may vary through all shapes to globose, with black, straight or recurved cirrhi. The lateral hairs are not numerous; encrusted clearly and evenly septate and tapering; olive-brown at the base, nearly 4μ in diameter, and becoming lighter in colour towards the tips, frequently collapsed. The terminal hairs are encrusted and roughened, dark brown to black, and about 4μ in diameter, and generally spirally coiled, irregularly septate, and with a few septate and spirally coiled branches.

When young the spores are hyaline, greenish, with granular contents; when mature, oval or almost spherical, sometimes apiculate, or rounded at both ends, 4 × 5μ in our type.

Milk Cultures.—Alkaline digestion.

Heat Tolerance.—Growth when heated to 60° C. No growth when heated to 70° C.

Salt Tolerance.—Slight growth in Czapek solution containing 5 per cent. NaCl. No growth when 10 per cent. NaCl is present.

pH.—When grown in Czapek solution containing 5 per cent. NaCl there was little or no change.

Gelatine.—Partial liquefaction.

Diastase Production.—Feeble.

DISCUSSION.

It is a well-known fact that salted butter is less liable to become mouldy than unsalted; and unsalted butter made from sweet cream may be regarded as a suitable medium for mould growth under favourable conditions.

While it is recognised that the heat tolerance and salt tolerance figures only hold good for the conditions under which they were carried out, the results obtained show the range that exists among the various species of fungi. *Oidium lactis* is killed when heated to 60° C., while some fungi are not killed at 75° C. Most fungi do not grow at 5° C., but a species of Penicillium, Fusarium, *Mucor corymbifer*, and *Sporotrichum carnis* grew when held at this temperature Practically all the fungi grew in Czapek solution that contained 10 per cent. NaCl, most of them were inhibited by the addition of 15 per cent. NaCl, and all were inhibited by the addition of 20 per cent. NaCl. The inference from this is that 2·3 per cent. NaCl, or over, is necessary in butter to inhibit the growth of fungi.

Since moulds are aerobic, they usually show their presence by discoloured patches on the surface, and reduce the market value of the butter. The present investigation shows the large number of species that may occur in butter and that can survive under unfavourable conditions, since all the fungi described

were found in butter taken from the interior of a 56 lb. box two weeks old, and that had, in many cases, been put in cold storage, and in no case held at a temperature exceeding 15° C. Although many of these fungi had previously been recorded as found in milk (2), it is regarded as unlikely that the butter was contaminated from this source, as the cream is pasteurised and cooled before churning, although it could occur with inefficient pasteurisation.

The pasteurisation temperature ranges from 85° C.–95° C., and no mould was found to survive this temperature. The probable explanation is that these types of fungi are widespread, and get into the cream either after pasteurisation, or during churning, or into the butter after manufacture. The water used for washing the butter may be a source of contamination, since it is sometimes stored in an uncovered tank. The churn is considered to be the chief piece of equipment responsible for mould trouble in the creamery. Crevices and cracks gradually develop in the wood and rollers, in which fungi can thrive, and only those who have tried can realise the difficulty of sterilising a churn.

Air contamination is another cause. Creameries are generally situated by the road-side, which increases the risk of contamination by air-borne fungal spores. In the creamery the machinery in motion keeps the air in circulation, and spores of fungi growing in damp or neglected places are blown about, and thus get into the cream or butter. The cream, after pasteurisation, is exposed to contamination from the air, since it flows over a water- or brine-cooler, and is further usually cooled in an open vat. The butter is exposed while being transferred from the churn to the boxes, and the packed boxes are left for a varying period of time standing on the floor before the lid is put on.

Owing to the provisions of the Dairy Produce Act, 1924, wood, parchment, and salt are considered to be negligible factors, unless they have been left exposed in a damp place.

Attention is drawn to the fact that when moulds were sent for confirmation as to species, those to whom they were sent remarked in many cases that, while they closely resembled a certain species, they did not conform altogether to the type species.

This is believed to show that the Irish fungi, as a result of insularity, have developed characteristics of their own.

Summary.

In the course of an investigation into the causes of deterioration of butter made from sweet cream, a study was made of the fungi found. The following were identified:—

(1) *Aspergillus fumigatus* Fres.
(2) *Aspergillus luteo-niger* Lutz
(3) *Aspergillus sydowi* Bainer and Sartory
(4) *Aspergillus terreus* Thom
(5) *Aspergillus glaucus* group Thom
(6) *Penicillium brevi-compactum* Dierckx var.

(7) *Penicillium johannioli* Zaleski
(8) *Penicillium cyclopium* Westling var.
(9) *Penicillium sartoryi* Thom
(10) *Penicillium spinulosum* Thom var.
(11) *Gliocladium* spp. Corda
(12) *Trichoderma lignorum* Tode
(13) *Graphium penicillioides* Corda
(14) *Coniosporium arundinis* Corda
(15) *Fusarium* spp. including *F. reticulatum* Mont.
(16) *Alternaria* spp.
(17) *Stemphyllium* spp. Wallr. including *S. ericoctonum.*
(18) *Torula* spp. Pers.
(19) *Phoma* spp.
(20) *Oidium lactis*
(21) *Acrostalagmus cinnabarinus* Corda
(22) *Botrytis cinerea* Pers.
(23) *Cladosporium* spp.
(24) *Mucor racemosus* Fres.
(25) *Mucor corymbifer* Cohn
(26) *Stysanus microsporus* Sacc.
(27) *Sporotrichum carnis* Brooks and Hansford.
(28) *Trichothecium roseum* Link
(29) *Chaetomium bostrychoides* Zopf.

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Plate 22.

Fig. 1A. Irregular head of *Aspergillus glaucus* var. showing branches from which secondary heads will be produced.
Fig. 1B. Later stage of similar irregular head showing appearance of secondary heads.
Fig. 1C. Warted spores of above.
Fig. 2. *A. fumigatus* head drawn to scale for comparison with *A. terreus*, fig. 3.
Fig. 3. Columnar head of *A. terreus* drawn to same scale as *A. fumigatus*, fig. 2.
Fig. 4. Diagram of arrangement of *A. fumigatus* showing flask-shaped vesicle and single row of sterigmata.
Fig. 5. Diagram of arrangement of *A. terreus* showing double row of sterigmata and spherical vesicle.
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Fig. 7A. Penicillus-like head of *Gliocladium* sp.
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Fig. 9C. Cladosporium-stage of *Graphium penicillioides*.

Fig. 10A. *Coniosporium arundinis* Corda spores.
Fig. 10B. Appearance of young fructification of *Coniosporium arundinis* Corda under high power.
Fig. 11A. *Fusarium* spore strain A.
Fig. 11B. *Fusarium* spore strain C.
Fig. 11C. Microconidial stage of *Fusarium* sp.
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Fig. 12A. Appearance of *Stemphyllium ericoctonum.*
Fig. 12B. Rounded mycelial cells.
Fig. 13. *Torula* sp., appearance under high power.
Fig. 14. *Chaetomium bostrychoides* Zopf. Appearance of perithecium.

Plate 23.

Fig. 1. Microphotograph of head of *Aspergillus fumigatus.*
Fig. 2. *Coniosporium arundinis* culture—showing streaked appearance due to acervuli.
Fig. 3. Microphotograph of *Alternaria* sp.
Fig. 4. *Stemphyllium ericoctonum* strain with small spores.

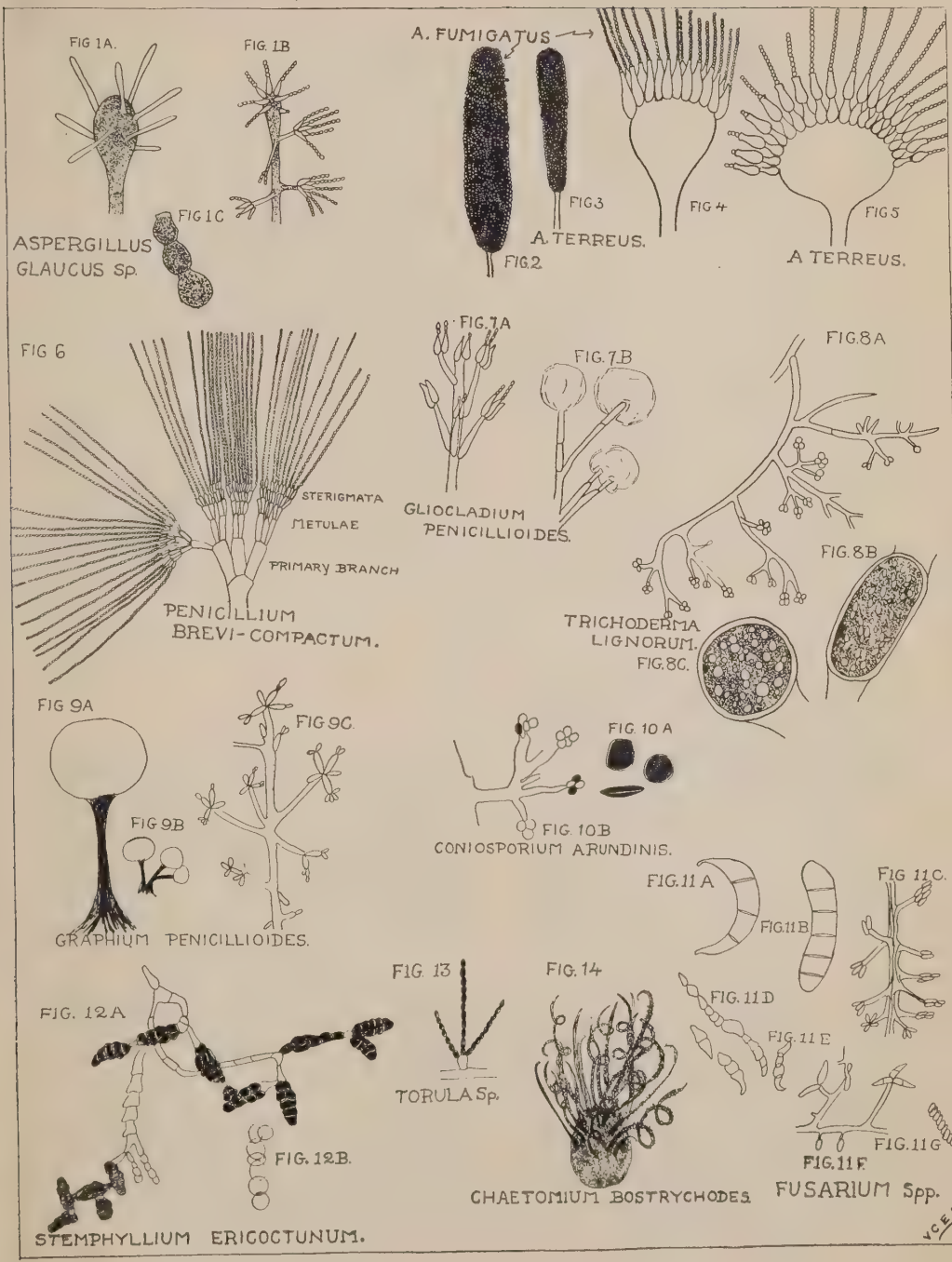
FIG 1A.
FIG. 1B
FIG 1C
ASPERGILLUS GLAUCUS Sp.
A. FUMIGATUS
FIG 2
FIG 3
A. TERREUS.
FIG 4
FIG 5
A TERREUS.
FIG 6
STERIGMATA
METULAE
PRIMARY BRANCH
PENICILLIUM BREVI-COMPACTUM.
FIG. 7A
FIG. 7B
GLIOCLADIUM PENICILLIOIDES.
FIG. 8A
FIG. 8B
TRICHODERMA LIGNORUM.
FIG. 8C.
FIG 9A
FIG 9B
FIG 9C.
GRAPHIUM PENICILLIOIDES.
FIG. 10 A
FIG. 10B
CONIOSPORIUM ARUNDINIS.
FIG. 11 A
FIG. 11B
FIG 11C.
FIG. 11 D
FIG. 11 E
FIG. 11 F
FIG. 11 G
FUSARIUM Spp.
FIG. 12 A
FIG. 12 B.
STEMPHYLLIUM ERICOCTUNUM.
FIG. 13
TORULA Sp.
FIG. 14
CHAETOMIUM BOSTRYCHODES.

FIG. 1.

FIG. 2.

FIG. 3.

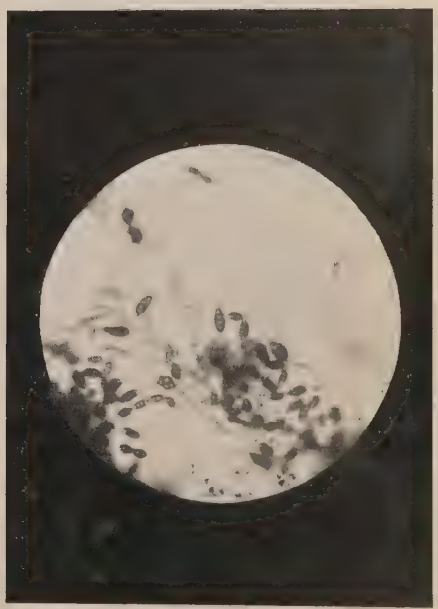

FIG. 4.

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